CHEMICAL EDUCATION

HERE'S HOW TO ENLIST YOUR BINOCULARS

The Navy needs every binocular it can get. If you have a Bausch & Lomb 6 x 30 or 7 x 50 binocular and will turn it over to the Navy for the duration, pack it carefully and ship to the Naval Observatory, Washington, D. C., or deliver to the nearest naval district headquarters. An identification tag bearing your name and address should be fastened securely to each instrument. Accepted binoculars will be acknowledged with a fee of one dollar and will be returned to you after the war if still in use.

The Navy is not authorized to accept gifts or free loans. Therefore, the binoculars are purchased for $1.00 and if they are available after the war they will be returned to the owner, in which case the $1.00 will constitute rental and appreciation charges. Commanding officers of naval vessels are requested to notify you of the ship aboard which your binoculars are in service.

They're in the Navy Now

SOMEWHERE on the high seas, with engines throbbing in the urgency of their mission, grim gray ships press forward in spite of the deadly perils of sea and sky.

On the bridges and look-out stations of such ships, brave men stand alert, searching the horizon—on guard against enemy attack. These are the men whose task it is to fight our sea battles and protect the ships which feed your sons and your brothers, your friends and fellow workers—clothe and arm America's expeditionary forces—strengthen and aid our allies.

You can help these men, and thus help to hasten the day of Victory, by sending them your binoculars for the duration.

Binoculars are among the many optical instruments of war that Bausch & Lomb is producing and helping others to produce. Today, Bausch & Lomb is working a full twenty-four hours a day, but even with its vastly expanded production program there is not room enough, nor time enough, to turn out all of the binoculars the Navy needs.

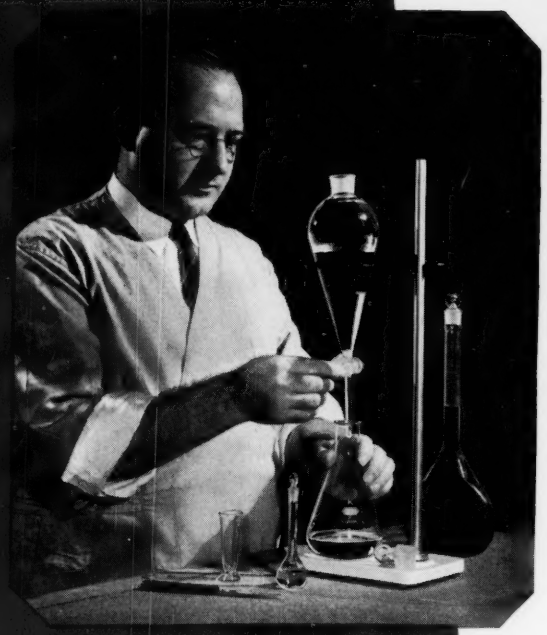
That is the problem you can solve—you and all the thousands of other owners of Bausch & Lomb 6 x 30 or 7 x 50 Binoculars. Your binoculars can help save American lives and American ships.

BAUSCH & LOMB
OPTICAL CO. EST. 1853

AN AMERICAN SCIENTIFIC INSTITUTION PRODUCING OPTICAL GLASS AND INSTRUMENTS FOR MILITARY USE, EDUCATION, RESEARCH, INDUSTRY AND EYESIGHT CORRECTION

BOSTON UNIVERSITY COLLEGE OF LIBERAL ARTS LIBRARY

The Chemist is Today's Crusader Against Shortage of Materials



Synthetic rubber is only one of the achievements of modern chemistry in developing alternatives to meet current emergency demands.

KIMBLE LABORATORY GLASSWARE fills requirements of today's chemical workers in *many* essential professions and industries. Consult leading laboratory supply houses throughout the United States and Canada for Kimble products to serve your own needs.

An Item From the Comprehensive KIMBLE LINE

29050-ST Funnel, Separatory, Squibb's, Pear Shaped, Kimble Brand, with ⅀ stopper and stopcock.

Capacity ml.	⅀ Stopcock Size	⅀ Stopper Size	Each
125	2	22	$1.40
250	2	22	1.60
500	4	27	1.90
1000	4	27	2.50
2000	6	38	3.50

Your dealer will be glad to supply further details, and to quote quantity prices.

29050-ST

For Assurance

You will be heartily welcome at our Booth No. 142 at the National Chemical Exposition, Hotel Sherman, Chicago, November 24 to 29, 1942.

The Visible Guarantee of Invisible Quality

KIMBLE GLASS COMPANY . . . . VINELAND, N. J.

NEW YORK • CHICAGO • PHILADELPHIA • DETROIT • BOSTON • INDIANAPOLIS • SAN FRANCISCO

Journal of CHEMICAL EDUCATION

PUBLISHED BY THE DIVISION OF CHEMICAL EDUCATION OF THE AMERICAN CHEMICAL SOCIETY

A. J. Currier, *Chairman* L. L. Quill, *Vice Chairman* P. H. Fall, *Secretary* C. E. White, *Treasurer*

OFFICIAL ORGAN OF THE DIVISIONS OF CHEMICAL EDUCATION AND HISTORY OF CHEMISTRY

INCORPORATING THE REPORT OF THE NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS

NORRIS W. RAKESTRAW
Editor

June Billhardt *Asst. to the Editor*
Harvey F. Mack *Business Manager*
Cyrus S. Fleck *Asst. Business Manager*
B. F. Gould *Advertising Manager*
C. L. Wells *Circulation Manager*

BOARD OF PUBLICATION

Stuart R. Brinkley, *Chairman*

J. C. Bailar P. H. Fall
W. L. Evans F. E. Brown

ASSOCIATE EDITORS

Hubert N. Alyea
Princeton University

Aubison T. Burtsell
College of the City of New York

Tenney L. Davis
Norwell, Massachusetts

Ed. F. Degering
Purdue University

William A. Felsing
University of Texas

Laurence S. Foster
Brown University

Malcolm M. Haring
University of Maryland

Philip A. Leighton
Stanford University

Laurence L. Quill
University of Kentucky

Elbert C. Weaver
Bulkeley High School
Hartford, Conn.

BUSINESS & PUBLICATION OFFICES
20th and Northampton Streets
Easton, Pennsylvania

EDITORIAL OFFICE
Metcalf Chemical Laboratory
Brown University, Providence, R. I.

ADVERTISING OFFICE
11 West 42nd Street
New York, N. Y.

VOL. 19 NOVEMBER, 1942 NO. 11

Frontispiece—Water Repellency XIII

Editor's Outlook 503

What's Been Going On 504

The History of Chemistry in South Carolina, *J. E. Copenhaver* 505

Frozen Assets: The Problem of Putting Chemical Knowledge to Work, *Byron A. Soule* 508

Rubber the Remarkable 509

Ceramics and Industrial Minerals in the War Effort, *Henry G. Fisk* 510

Simple Projection Manometer for Lecture Demonstrations, *John W. Moore and Carl M. Furgason* 513

High Polymers and New Rules, *S. Weiner* 514

An Automatic Buret for Dispensing Volatile Reagents, *John W. Murray* 516

Courses in Advanced Analytical Chemistry. I. Texts for Courses in Applied or Technical Analysis, *Philip J. Elving* 517

Natural and Synthetic Rubbers, *Harry L. Fisher* 522

Semimicro Equipment for the Elementary Laboratory, *Shirley Gaddis* 530

A Simplified Electronic Thermoregulator, *Warren E. Gilson and Harold A. Woosler* 531

Revision of the Indicator Method of Classifying Acids and Bases in Qualitative Organic Analysis, *David Davidson* 532

A Simplified Electrosmosis Apparatus, *Jermain D. Porter* 533

Opportunities for Women in Chemistry, *Lois W. Woodford* 536

High-School Chemistry
Refrigeration, *Ward V. Evans* 539

Division of Chemical Education of the American Chemical Society 544

Out of the Editor's Basket 545

Letters 547

Lecture Demonstration of X-Rays and Cathode Rays, *Charles L. Christ* 548

REPORT of the New England Association of Chemistry Teachers 549

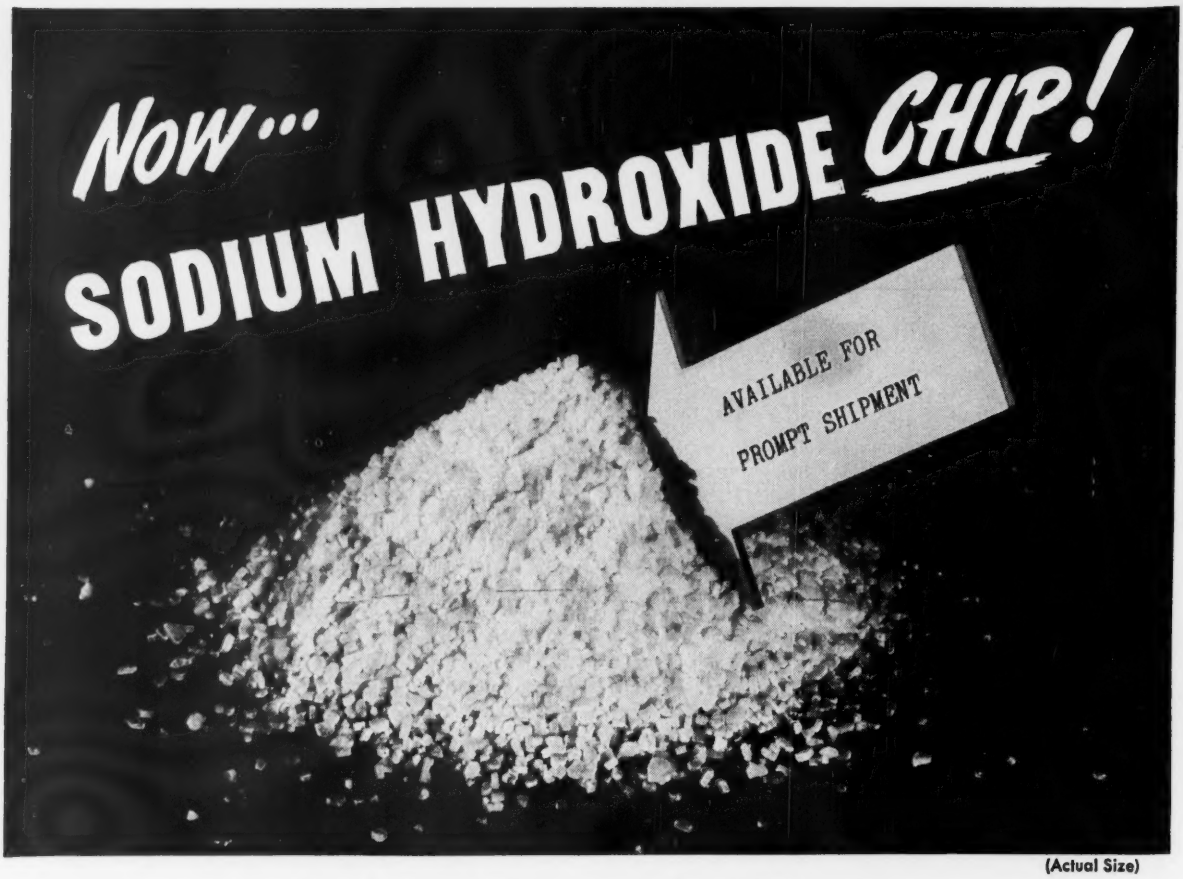
Recent Books 551

Trade Announcements XVI

Subscription Price: $3.00 per year; Canada $3.50; other countries $4.00. Issued monthly. Single copies of issues in current year, 50c each; all other single copies, one dollar. Foreign remittances must be accompanied by International Money Order.
No claims for copies of journals lost in the mails can be allowed unless such claims are received within sixty (60) days of the date of issue and no claims can be allowed for issues lost as a result of insufficient notice of change of address.
Manuscript for publication should be directed to the editor. Prospective authors are urged to avoid diffuse writing and to observe the forms outlined in our Notice to Authors of Papers as it appears on page XIV of the January, 1942, issue.
Entered as second-class matter, January 31, 1924, at the Post Office at Easton, Pa., under the act of March 3, 1879. Accepted for mailing at special rate of postage provided for in Section 1103, Act of October 3, 1917, authorized January 31, 1924.
The JOURNAL OF CHEMICAL EDUCATION *is indexed in the Education Index, Industrial Arts Index, and, in part, in the Quarterly Cumulative Index Medicus*

COPYRIGHT, 1942, BY DIVISION OF CHEMICAL EDUCATION, AMERICAN CHEMICAL SOCIETY

BOSTON UNIVERSITY
COLLEGE OF LIBERAL ARTS
LIBRARY



(Actual Size)

Baker & Adamson Announces Sodium Hydroxide CHIP—

A NEW CONVENIENT FORM in Reagent A.C.S. and U.S.P. Grades

Baker & Adamson is pleased to announce the availability of Sodium Hydroxide in a new physical form—Chip—in both Reagent A.C.S. and U.S.P. grades.

Sodium Hydroxide *Chip,* aside from being economically advantageous to use, merits the attention of industrial, college and research laboratories, as well as those manufacturers whose processes require material of these purities, for these additional reasons:

★ Easily soluble, because of its small but uniform particle size.

★ Convenient to weigh and handle.

★ Fuses readily with other chemicals.

★ Can be readily ground to powder form.

When Ordering Sodium Hydroxide, Specify Baker & Adamson CHIP

Reagent A.C.S. Grade Code 2249	*U.S.P. Grade* Code 2251
¼, 1 and 5 lb. bottles	¼, 1 and 5 lb. bottles
10 and 25 lb. cans	10 and 25 lb. cans
100 and 400 lb. drums	100 and 450 lb. drums

WRITE TODAY FOR PRICES ON THE NEW CHIP GRADES!

SETTING THE PACE IN CHEMICAL PURITY SINCE 1882

B&A STANDARD OF PURITY

BAKER & ADAMSON *Reagent Chemicals* AND *C.P. Acids*

Division of GENERAL CHEMICAL COMPANY, 40 Rector St., New York

Technical Service Offices: Atlanta • Baltimore • Boston • Bridgeport (Conn.) • Buffalo • Charlotte (N. C.) Chicago • Cleveland • Denver • Detroit • Houston • Kansas City • Milwaukee • Minneapolis New York • Philadelphia • Pittsburgh • Providence (R. I.) • St. Louis • Utica (N. Y.)

Pacific Coast Technical Service Offices: San Francisco • Los Angeles

Pacific Northwest Technical Service Offices: Wenatchee (Wash.) • Yakima (Wash.)

In Canada: The Nichols Chemical Company, Limited • Montreal • Toronto • Vancouver

Courtesy of E. I. du Pont de Nemours and Company

Water Repellency

This is how a fabric processed with a water-repellent reacts toward globules of water.

BOSTON UNIVERSITY
COLLEGE OF LIBERAL ARTS
LIBRARY

WELCH SPECTROMETER

R. W. Wood Design

No. 3693

ACCURACY UNDER 50 ANGSTROMS

ADJUSTABLE SLIT

SCALE 4000 TO 7600 ANGSTROMS

REPLICA GRATING FROM MATRICES RULED BY DR. R. W. WOOD

Precise yet Inexpensive

IDEAL FOR QUICK AND PRACTICAL TESTING AS WELL AS FOR STUDENT USE

CONVENIENT AND PORTABLE.

In some laboratories as many as 15 to 20 of these spectrometers have been installed to take care of the constant need for this useful instrument.

Spectrometric measurements can be made on a moment's notice with assured accuracy less than 50 angstroms, and mounting is so arranged that the spectrometer can be held in the hand and used in almost any position in the laboratory.

PARALLAX IS COMPLETELY ELIMINATED through ingenious arrangement of the positions of the replica in the eyepiece, and of the slit and scale.

BRILLIANT SPECTRA are easily observed from vacuum tubes, or by the ordinary flame method without darkening the room. The relationship of the angle of diffraction and the Angstrom scale is easily explained.

NO LIMIT TO ITS ADAPTABILITY. Can be used to decided advantage in making rapid observations in complicated laboratory operations where it is impractical to set up an ordinary spectrometer.

FILTER HOLDER AND ADJUSTABLE SLIT. A special bracket is provided for holding any desired filter in front of the slit, and a selected cobalt filter is supplied with the instrument for studying the absorption lines in the solar spectrum.

No. 3693—SPECTROMETER. Complete with manual outlining and giving diagrams for numerous laboratory applications. . . . . **Each**

LIGHT ATTACHMENT — aluminum casting, with flash-light bulb and battery for dark room use to illuminate scale. . . . . **Each $4.00**

$25.

W. M. WELCH SCIENTIFIC COMPANY

Established 1880

1516 Sedgwick Street **Chicago, Illinois, U. S. A.**

Editor's Outlook

CHEMISTS, like all other people of stout and true heart, want to do their part in this war. They would much prefer to do it in the way for which they have been trained, and in which they believe they can be most effective, but, failing that, they are apt to do it in the way that first comes to hand. It is not only the draft boards that are driving young men out of the production army into the combat army, but also a sense of disillusionment. This sense may be founded on mistaken reasoning, but it has all the power of disillusionment, nevertheless.

I hear of young chemists who have left college and gone into industry with a strong patriotic desire to put their hard-won scientific training at the service of their country. Soon they find themselves assigned to jobs which—they feel—could be done by almost anyone after a few days or a few weeks of training. Seeing nothing ahead, they quit, and rush off into the Navy or Air Corps.

The responsibility for this situation is, of course, divided. First, the "indoctrination" of these men in college has been perhaps a bit too effective. They must realize that every young A.B. or B.S. in chemistry is not going to be given a captain's commission in the production army at his first enlistment. He will find that the school of the soldier, in the combat army too, will include many a menial task before a chevron is won, and for every soldier who gets a shot at the enemy, there will be several behind the lines doing less spectacular work. Furthermore, no young man, on undertaking a new job, is in a position to judge his present or potential value to industry; only his superior can do so, and his opinion should be trusted.

And here the responsibility shifts. If industry loses its chemists it will have itself to blame, in large part. Already too supine and non-resistant an attitude has been taken toward the often unreasonable actions of an unselective Selective Service. Like everyone else, industry has been too content to allow the Army and no one else to say what shall be done with man power. It has been too preoccupied with the pressing job of production—its most important job, to be sure—to have time to think who is going to do the producing, particularly day after tomorrow. Too much labor overturn has always been costly to industry; just now it may be disastrous, particularly in the ranks of the technically trained. Somehow these men must be made to *want* to stay on the job.

No doubt this is outside industry's sole province; since it involves the patriotic motive it has something to do with national morale. Certainly it is more than the hiring-firing idea of employment.

As long as the production army has no organization, no uniform, no insignia, no glamor, it will be a poor competitor with the combat army for enlistment and service. Its popular standing and personal appeal are in poor ratio to its real importance in the war effort. If the already overworked minds in our Government can find no better way to remedy this situation, perhaps industry can. It certainly had better.

A very promising plan was indeed presented to the War Manpower Commission some time ago. A plan which would have supplied industry with at least a moderate supply of trained personnel. This would have been accomplished by dividing the "enlisted reserve" in the higher educational institutions between Army, Navy, and Industry, by paying for the support of students during this training period, and by obtaining assurances that each man would serve in that branch to which he was assigned, on the basis of his demonstrated capabilities. Alas, it was too good to be true.

CEILING and visibility in our higher educational institutions become lower and shorter. We can see less and less far ahead. It is by no means certain that students—those fit for military service, that is—will be allowed to remain in college beyond the first year or two. Not even the Army, which calls the turn in this matter, is very certain. Thinking about ten million men in the future must indeed be very distracting when it comes to making a decision in the immediate present.

However, the smart institutions are laying their plans and seriously studying how to change their curricula so as to present in the first year or two a maximum of whatever the particular institution thinks a young man should have in order to face his personal problem in relation to the war.

Liberal arts colleges are perhaps less worried about changing the curriculum than about keeping any kind of a student body. For the most part, they conceive their mission to be teaching the student how to learn, and they believe that the Army will soon enough tell him what to learn—as it probably will.

Technical schools, and technical departments in other institutions, believe that their courses themselves are a direct contribution to the war, in the form of training for industry or the military services, and they are planning to streamline their offerings and condense the more essential parts of a four year course into two or three. Nevertheless, it is surprising what can be done in chemistry, for example, if one peels off all the trimmings down to the basic courses in chemistry, physics, and mathematics. Two years will be ample for a pretty well *trained* chemist. Not a very well *educated* one, perhaps, but education is a leisurely pursuit, and maybe this is no time for leisure. The more serious question, however, is whether our young men and women can absorb it that fast. The experience of wartime training in other fields should give us hope, at least. Young people have been rising to the occasion surprisingly well.

BOSTON UNIVERSITY
COLLEGE OF LIBERAL ARTS
LIBRARY

What's Been Going On

Versatile Scavenger

Reprinted from Industrial Bulletin of Arthur D. Little, Inc., September, 1942.

TO MATERIALS, as to men, the emergencies of war present a fresh chance to show "what they've got." Such an opportunity is being offered to calcium, a minor but interesting metal, which, for the first time, is being produced in commercial quantities in this country. Until 1939, when a plant was erected for its production in Michigan, the United States was entirely dependent on France for imports, which were then only about 41,000 pounds a year. Demand is now considerably greater. For comparison, the United States imported 3,180,000 pounds of gold and 7,400,000 pounds of silver in 1937.

The limited but growing consumption of calcium can certainly not be laid to the rarity of its ores, including chalk, marble, gypsum, and fluorspar. It is the fifth most common element in the earth's crust. Calcium is also vital in animal metabolism as the principal constituent of bones. Like strontium and barium, an alkaline earth metal, it is active chemically, and at temperature approaching its melting point of 810°C. it will react with many elements, including nitrogen, hydrogen, and any gas containing oxygen. This chemical promiscuity is the reason for many of its industrial applications, but is also a major source of difficulties encountered in its preparation.

Many methods of obtaining the metal are known, but the one used commercially is its electrolysis from melted calcium chloride. Theoretically simple, this procedure is so difficult to control in practice that calcium production outside of France and Germany, where skilled but cheap labor is available, was long discouraged. The melting point of calcium is only 38°C. above that of the salt from which it is obtained; the calcium must be removed as quickly as it is formed and protected from the chlorine liberated at the anode. American production, however, is from larger cells than those used in Europe and is based on research into the details of the process. It is believed that the industry is sound enough technically to survive European competition after the war.

Calcium can decarburize, deoxidize, and scavenge steel alloys; desulfurize petroleum products; and dehydrate alcohol and organic solvents. Calcium cannot replace magnesium in removing bismuth from lead, but half of the magnesium can be replaced by calcium if calcium is cheap enough. Metallic calcium is widely used in so-called "getter" mixtures for removing the last traces of gases from vacuum tubes and other high-vacuum apparatus, for it will combine readily with nitrogen as well as oxygen. This ability of calcium to form nitrides is used to separate nitrogen from argon. Calcium will also react with hydrogen to form calcium hydride. When this compound is heated to above 300°C. it gives up hydrogen in the atomic or "nascent form," in which it is much more active than the usual molecular state. The powerful reducing effect of nascent hydrogen is used in separating many metals, such as titanium, zirconium, thorium, and uranium from their stable, refractory ores, and has simplified the alloying of these elements with copper and nickel. Metallic calcium can also be used as a strong reducing agent.

Added in small amounts, calcium will improve the structures of many alloys. Added to magnesium base alloys in amounts up to 0.25 per cent, calcium improves the tensile strength and ductility of some wrought alloys and improves the surface and inhibits oxidation during casting of casting alloys. It has, however, other characteristics which are not always favorable, so that it has attained only a limited use in magnesium alloys at present. Calcium is used in the preparation of high-lead copper-bearing metal alloys, and its use as a hardener for lead in amounts up to 0.25 per cent has given encouraging results in cable sheathing and battery plate. Added to lead, its most notable results are a higher fatigue strength and tensile strength than is obtained with the widely used one per cent antimony-lead alloys. Cable sheathing and battery plates are consistently two of the largest uses for lead, and calcium additions are of considerable interest in both fields. At present, however, the calcium is obtained from calcium-lead hardeners in which the calcium is deposited by chemical or electrolytic means, but the addition of metallic calcium is the simplest method and may be used if the price of calcium is further reduced. The use of calcium in making stainless and other high-alloy steels gives a particularly clean product. Because of its low specific gravity (lighter than magnesium) and the rapidity with which it oxidizes at high temperatures, its addition to steel melts is a problem. Calcium is obtainable in cored cylinders which can be slipped over an iron rod and thus plunged below the surface of the molten metals. Another method is to shoot lumps of calcium into the melt with a compressed air gun.

More active chemically than either barium or strontium, and cheaper on a pound basis, calcium is by far the most important of the alkaline earth metals. The alkali metal sodium is cheaper still and more active chemically, but because of its very low melting point it cannot compete with calcium for many metallurgical applications. For material of 97 per cent to 98 per cent purity, calcium is now selling for about $1.25 per pound in ton lots. It is available in the form of crude salt-covered "carrots," the term applied to the rough, truncated cones in which the metal is deposited in the bath, as chips and turnings, and in a limited number of cast forms. The entire foundry procedure must be carried out under inert or reducing blankets of gases and fluxes. By distillation and condensation of electrolytically deposited calcium, metal of very high purity may be obtained.

Junior Metallurgists Needed by Civil Service

INCREASING numbers of scientifically and technically trained men and women will be required for the War effort this year and next. Junior Metallurgists are urgently needed to conduct investigative, developmental, or production work in various branches of metallurgy; to assist in the design, construction, installation, and operation of metallurgical equipment, or to perform metallurgical work in the recovery or fabrication of metals.

There is provision for the acceptance of applications from college senior or graduate students who expect to complete the required courses within six months after filing applications.

In addition to the positions which pay $2000 a year, there are a large number of vacancies in the subprofessional positions at $1800 and $1620 a year.

Announcements and application forms for these and other chemical openings may be obtained at any first- or second-class post office or from the Civil Service Commission, Washington, D. C.

The History of Chemistry in South Carolina[1]

J. E. COPENHAVER

University of South Carolina, Columbia, South Carolina

THE FIRST permanent settlement in South Carolina was made in Charles Town in 1670. Throughout its long history as a Province and a State, South Carolina has been primarily agricultural and only within the last half century has there been a trend toward industrialization, the tempo of which has increased each year. To trace the history of chemistry here, one must take into consideration several phases of agricultural and industrial developments, which have had a direct or indirect bearing upon the subject in question.

The early commercial development of South Carolina was very similar to that of the other southern colonies, in that South Carolinians utilized such natural resources as they had, while experimenting to determine which commodities could be produced most profitably.

Native timber has been, and is, South Carolina's greatest natural resource. Its principal uses have been for building material and fuel. From the southern pines, also, turpentine and rosin are obtained. Other than their separation by the "turpentine stills" scattered over the state, there has been no further conversion of these products.

One South Carolinian created a new use for the southern pine by discovering a process for its conversion into paper. James L. Coker, Jr.,[2] of Hartsville, a graduate of Stevens Institute of Technology in 1887, became interested in the production of paper from southern pines because of their abundance. He perfected a process for the manufacture of unbleached paper by the sulfite method and marketed it in 1893. He received several patents on the process, the main one having been granted in 1906. The pine trees were cut, allowed to remain in the woods from four to twelve months to reduce the resinous matter, then barked, hearted, and the sap wood used to make paper. This process was used by the Carolina Fiber Company at Hartsville until 1926. During the latter years, the young trees were used without removing the heart. Since 1926, the company has changed to the use of hard woods. As concluded by Harold L. Murdock in his article on this industrialist: "James L. Coker pioneered on three counts: He was the first to manufacture from southern pines, (*a*) chemical pulp, (*b*) unbleached paper, and (*c*) groundwood pulp."

Because of the enormous reserve of southern pines, two large pulp and paper mills have located in South Carolina within the last ten years: the Southern Craft Corporation at Georgetown; and the West Virginia Pulp and Paper Company at Charleston, the latter company bringing along its research laboratory. The Sonoco Products Company, Hartsville, manufacturers of paper cones for a number of years, established in 1934 the first industrial research laboratory in the state. Two plywood and thirteen veneer plants, using hardwoods, are now located in South Carolina. Unless controlled by proper scientific supervision, South Carolina will deplete her greatest natural resource.

South Carolina has suffered from the lack of extensive mineral deposits. Gold has been mined intermittently for the last two hundred years and one sizeable mine is in operation at present. Kaolin occurs east of the fall line and this state ranks second in its production. There are abundant clays and shales for bricks, and sand for glass, there being one glass factory at Laurens. A few other minerals are found to a small extent. The one mineral which has had a greater effect chemically than any other is phosphate rock. It was discovered near Charleston in 1859 by Dr. C. U. Shepard, Sr., who gave a report upon his findings, showing its similarity to the Sombrero "rock" guano before the South Carolina Medical Association.[3] Owing to the intervention of the Civil War, this important discovery was overlooked and phosphate rock was re-discovered in 1867 by Dr. St. Julien Ravenel.[4] This was the first native bone phosphate rock discovered on the North American continent and was the most abundant and easily mined in the world at that time. The rapid growth of this industry is indicated by the fact that from 1873 to 1883, South Carolina was the biggest producer of land and river rock phosphates. The presence of phosphate rock led to the establishment of fertilizer companies, so that superphosphates were also manufactured. From 1867 through 1883, a total of 2,299,000 tons of phosphate rock were mined, averaging about $6 per ton, or $16,194,000, with royalties to the state of $1,229,170. It has been estimated that during the above-mentioned period "about $50,000,000 was brought into the state by this industry in the mining and manufacture of fertilizer." Beginning with 1884, the industry declined, due to overproduction, short-sightedness of politicians in

[1] Presented before the Division of the History of Chemistry at the 103rd meeting of the A. C. S., Memphis, Tennessee, April 21, 1942.

[2] MURDOCK, "James L. Coker, Jr., pioneer producer of pulp and paper from southern pine," *Ind. Eng. Chem., News Ed.*, **18**, 447 (1940).

[3] MAPPUS, "The phosphate industry in South Carolina," unpublished thesis, University of South Carolina Library, Columbia.

[4] PRATT, "Ashley River phosphates," Inquirer Book and Job Printing Company, Philadelphia, **1868**; HOLMES, "The Charleston phosphates," Holmes Book House, Charleston, **1870**; CHAZAL, "The century in phosphates and fertilizers," Centennial Edition, *News and Courier*, Charleston (April 20, 1904). Also in pamphlet form.

levying excessive taxes on "the goose that laid the golden egg," and to the discovery of richer and more easily mined phosphates in Florida in 1888, and in Tennessee in 1894. In 1891, Charleston was the leading fertilizer manufacturing city in the United States. Mining of South Carolina rock rapidly declined and ceased in 1920. Since the Florida rock analyzed about ten per cent higher than that in South Carolina, the fertilizer companies could afford to import the phosphate, so that Charleston continues to be one of the largest fertilizer manufacturing cities in the United States. It is interesting to note that South Carolina uses more fertilizer than any other state in the union.

Cotton, rice, and indigo were introduced into the Province of South Carolina about 1690, each commodity being developed by the plantation owners at different periods, one supplanting the other to a certain extent, depending upon the ease of production and the returns derivable therefrom. No attempt will be made here to discuss in detail each of these, or to evaluate their influence upon the cultural, political, and economic background of the state. Indigo and rice flourished for a time and vanished. Cotton, for over a hundred years the principal staple crop, is gradually being supplanted by greater diversification of agriculture. Not only has it been the principal cash crop for the farmer, but it has been the cause of scores of cotton mills being established here, as well as several dyeing plants, which have laboratories employing many chemists. Cotton is consequently the backbone of the State's present industrialization. Not so many years ago, the seeds of the cotton were thrown away. Now, several mills are located here which express the oil, although all of it is exported for processing.

The history of indigo is very interesting to the chemist.[5] Although the indigo plant is indigenous to South Carolina, cultivated varieties were introduced which would give a greater yield of dye. Little attention was attached to it until 1741–42, when its cultivation was encouraged and by 1747–48, it was exported to the amount of 134,118 pounds. England, in order to be free from purchasing the dye from France, her commercial rival, in 1748 offered a bounty of six pence (about twelve cents) on each pound of indigo produced in her colonies. This was reduced to four pence in 1764 because of the large amount being shipped to her. This added stimulation, along with some lean years when rice was cheap, due to overproduction, increased the cultivation of indigo to such an extent that by 1775 the exportation from Charleston alone amounted to 1,150,662 pounds, valued at $1.10 to $1.20 per pound in our present currency. The loss of the bounty and European markets as a result of the Revolution, and the stimulation of cotton production by the invention of the gin, caused the culture of indigo to decline rapidly. It had practically faded from the picture before its synthetic production in 1868.

[5] COPENHAVER, "The culture of indigo in the provinces of South Carolina and Georgia," *Ind. Eng. Chem.*, **22**, 894 (1930).

Rice followed the same general pattern as indigo but was spread over a longer period. It received its death blow about the turn of the last century, because of rice production in Texas and Oklahoma, and because of tropical storms which wrecked the dykes of the rice fields. Silk culture was also attempted, but other profitable commodities could be grown more easily. Mulberry trees for silk worms were planted throughout the Province. In 1755 Ex-Chief Justice Pinkney presented the Prince of Wales with a silk damask woven from silk grown on his plantation and dyed with South Carolina indigo. As much as 10,000 pounds were shipped to England in 1759.[6]

During the early days of science in this country, chemistry was placed under the general heading of "Natural Philosophy." One holding such a chair was supposed to teach two or more of the sciences, with possibly Greek or Latin thrown in for good measure. It was not until several years after the Civil War that any college in South Carolina had an instructor devoting all of his time to teaching pure chemistry. Many of our earlier chemists first took a degree in medicine and often, when they went to Europe for further medical study, came under the influence of some noted teacher of chemistry and changed their course of concentration. Such was the case of J. Lawrence Smith,[7] 1818–83, who was born in Charleston, studied at the University of Virginia, and took his M.D. degree at the Medical College of South Carolina, where his chemical interest was shown by submitting "a very interesting thesis" on "The Compound Nature of Nitrogen." In his advance study in Europe, as a roving student, he came under the dynamic influence of Liebig. When he returned to Charleston to practice medicine, his patients may have suffered because Dr. Smith was making analyses of limestone, marls, and soils of the vicinity, as well as investigating and simplifying methods of analysis. During his entire active life, he was primarily interested in analysis. It was while teaching at the University of Virginia that he published, in 1853, his article on alkaline silicates.

Another Charlestonian who followed the same general pattern of study was Dr. Lewis Reeve Gibbes,[8] 1810–94, who was graduated at the South Carolina College, now the University of South Carolina, in 1829, remaining there for some years to assist Thomas Cooper in chemistry. He took his M.D. degree at the Medical College of South Carolina in 1836 and spent one year in Paris, where he was influenced by the teaching of such men as Dumas, Pouillet, and Dulong to continue chemistry as a profession. He taught chemistry at the College of Charleston from 1839 to 1894, during which time he also taught mathematics, astronomy, physics, and mineralogy, publishing articles in each field. His

[6] WALLACE, "The history of South Carolina," American Historical Society, Inc., New York, **1934.**

[7] SILLIMAN, "Sketch of the life and scientific work of Dr. John Lawrence Smith," National Academy of Sciences, Washington, D. C., April, 1884.

[8] TAYLOR, "Lewis Reeve Gibbes and the classification of the elements," J. CHEM. ED., **18,** 403 (1941).

greatest publication was his "Synoptical Table of the Chemical Elements," presented before the Elliott Society of Charleston in 1875, but which, through lack of funds, was not published until 1886. This important contribution was recently brought to light by Wendell H. Taylor, who showed that Dr. Gibbes derived his classification independently. Had it been published in a nationally known journal, it would have received due recognition for originality of thought.

Among his many other accomplishments, Thomas Cooper, M.D., spent a considerable part of his life studying and teaching chemistry. That stormy petrel of many political battles in England and the United States, a close friend of Joseph Priestley in whose home he lived for a time, protégé of Thomas Jefferson, professor of chemistry at Dickinson College and the University of Pennsylvania, he came to South Carolina College in 1819 to occupy the chair of chemistry. Before he had finished his first year, he was elected to teach mineralogy and geology and upon the death of President Maxcy, Cooper succeeded to the presidency. During his tenure as president, he retained the professorship of chemistry and also taught belles lettres, criticism, logic, and political economy. Because of religious and political views, he was forced to resign in 1834. Dumas Malone,[9] summarizing the public life of Cooper, states: "Perhaps no man of Cooper's generation did more than he to advance the cause of science and learning in America . . . . In chemistry, geology, and economics, he was distinctly a pioneer."

Many other versatile and distinguished college teachers in South Carolina during the nineteenth century could be singled out, but space prevents. Dr. William B. Burney, for instance, a student of "dear old Bobby Bunsen," taught at the University of South Carolina for fifty-one years, 1880–1931, and was the first teacher in that school to devote all of his time to chemistry. As a general rule, teachers were then so overloaded with pedagogical duties that they had little time for research. Too much praise cannot be bestowed upon that early group of natural philosophers who were masters in two or more fields of science. Since we do not understand the many difficulties under which they worked, we are wont to criticize when we should stand in reverence. Their main product was students, who went to northern schools for advanced study and generally settled there because of the lack of industrial employment in the South. Teaching was about the only occupation for a chemist to follow in the South. This heavy exportation of the best chemical students from our state continues to a large extent and can only be relieved by establishing chemical industries within our boundaries. The optimum condition would be an equal flow, North, South, East, and West, to give an exchange of ideas and opinions, which would lend support to a greater unified nation. With this increased chemical industrialization, there will follow more advanced teaching in our colleges and universities, as well as the establishment of research laboratories.

Up until the Civil War, Charleston was known as the cultural center of the South. As was the case with other cities and towns during the ante-bellum days, there were organized groups or societies where the best minds of the day exchanged ideas. The Medical Society of South Carolina, organized in 1789, was instrumental in starting the South Carolina Medical College in 1833. The Charleston Library Society was formed in 1773, and, in order to have a place to house their specimens, established the first museum in the United States. Chemistry was included in natural philosophy, and some of the foremost naturalists of the country were among these societies scattered throughout the state. Their number and influence was such that, at Agassizi's suggestion, the American Association for the Advancement of Science met in Charleston in 1850.

Because of the destructiveness of the Civil War and the dire poverty following it, this cultural center, as well as others, was practically destroyed. Recovery was very slow, but South Carolina is gaining gradually some of the former prominence among her sister states. Chemistry is, and will continue to be, a valuable aid in this recovery.

In 1800, there was not a single college in South Carolina teaching chemistry. If an examination is made of the founding of academies, colleges, and universities in the eastern United States, it will be found that there was a great awakening of educational thought during the first three-quarters of the nineteenth century. This did not reach the secondary schools until the latter part of the nineteenth and the first part of the twentieth centuries. The sciences had to fight for their places in the college and high school curriculums, since there was always the struggle between minds relative to the merits of a classical and scientific education. That they have succeeded is indicated by the fact that there are two universities and sixteen white colleges, as well as six Negro colleges, four white and six Negro junior colleges, in which chemistry is taught at the present time. As a rule, chemistry was not taught in the high schools until after 1900. The first chemistry taught in the Columbia High School was in 1902 by Henry C. Davis, now Professor of English at the University of South Carolina. At the present time there are 163 high schools, as well as a number of orphanages, offering chemistry as a main subject.

The South Carolina Academy of Science, in which chemists have always taken an active part, was organized in 1924. The South Carolina Section of the American Chemical Society was organized in 1926 with about twenty-five members. This membership has gradually increased until there are now seventy-two, with very few chemists in the state as non-members.

Chemistry in South Carolina has thus passed through some dark days. Chemically, we are on the threshold of a new era. Many signs point to an unparalleled chemical development within the state in the future.

[9] MALONE, "Public life of Thomas Cooper," Yale University Press, New Haven, Connecticut, 1926, p. 400.

Frozen Assets: The Problem of Putting Chemical Knowledge to Work[1]

BYRON A. SOULE *University of Michigan, Ann Arbor, Michigan*

THE RESEARCH chemist is primarily a laboratory worker. He uses apparatus, frequently of his own construction, to test ideas for obtaining desired information. He spends years in acquiring manipulative skill and learning how to compel substances to obey his will. In addition to the training acquired, often the only product of a long and arduous search is a few grams of some compound or a page of hastily written notes confirming the published report of someone else. This experimental procedure is expensive, time consuming, and wasteful of materials. Any scheme for avoiding any part of it deserves careful consideration. The most obvious one is adequate library research.

During the past 280 years[2] several million reports have been published dealing with only positive results. In the last decade *Chemical Abstracts* has been listing annually an average of almost 40,000 printed papers and 20,000 patents with each subject index containing over 150,000 entries. So many manuscripts are now sent to the various journals of our one organization, the American Chemical Society, that available space is sufficient for the publication of only two-thirds of them. In addition to this volume of primary source material there are the secondary aids, condensations, etc.

Thus we have in print a vast amount of valuable information available to the laboratory worker—available if he knows where and how to find what he needs. The curious fact is that his laboratory training receives much attention while the acquisition of library skill is considered a side issue, something to be easily picked up by himself without instruction. Unaware of the existence of many excellent bibliographical tools and naïvely oblivious to the vagaries of indexes, he frequently spends valuable time repeating the work of others, using methods and apparatus long since discarded for reasons given in their buried reports.

Until the time arrives when we can find all useful information in one handbook we must either muddle along as we are doing, make the acquisition of library skill an essential part of the training of every research man, or establish an intermediary, the library technologist, well grounded both in chemistry and library reference work. Industrially, the time is fast approaching when the tremendous spread between basic cost and selling price must disappear. Instead of closing the laboratory, more funds must go to support more efficient research. Therefore, as the result of economic pressure alone, it seems logical to assume that the first alternative is already obsolescent, the second doomed through emphasis on increased specialization.

Several decades will undoubtedly pass during which the laboratory worker and the library expert must share the responsibility for searching the literature. Naturally the situation should be clearly reflected in the two expense accounts. If the library actually contains needed data that are not placed at the disposal of the research worker, the extra, unnecessary expense incurred by the laboratory in experimentally securing those figures should be charged against the library. On the other hand, when it produces information that saves much time and material in the laboratory the library should receive a commensurate credit entry.

Let there be no misunderstanding. The technical library expert is here advocated on a service basis. His function is to place before the experimenter all information pertinent to his work, to help eliminate the unnecessary repetition of operations and thereby promote progress of the research problem. He realizes that the library is not merely a collection of books, but also a storehouse of ideas entombed in words chosen by a succession of at least three others, *viz.*, the original author, the abstractor of his paper, and the indexer of the abstract journal. Consequently, if well trained for the work, by analyzing, particularizing, and generalizing the problem in hand, the librarian can quickly determine where to look, what to seek, and how to search. He is in fact just as skilled in the use of reference tools as an analyst in the use of a balance. Most emphatically he is not a librarian in the ordinary sense of the word; he is a user, rather than a guardian, of books. He is familiar with the more important foreign languages and, incidentally, has some ability as a mind reader and detective.

Before starting any major library search the technologist carefully plans his preliminary attack, having found it essential to understand exactly what is wanted and for what purpose. This gives him a notion of his own grasp of the subject and the status of its literature, both important factors in the initial approach. If the subject is old and the literature extensive, an encyclopedia article or bibliography in a standard reference book may be indicated. On the other hand it is possible that the discussion of a recent development is to be found only in the original article in the form of a patent, not a journal report. Fehling's "Handwörterbuch," for example, contains a good summary of the literature on zinc and a bibliography of some two thousand references, whereas the published data on the direct catalytic conversion of benzol to phenol are meager.

[1] Presented before the Division of Chemical Education at the 104th meeting of the A. C. S., Buffalo, New York, September 9, 1942.

[2] The Royal Society received its charter in the early 1660's.

The place to look for information is largely determined by the nature of the problem. One of the elementary lessons to learn is that the subject index of an abstract journal is not always the first and only source to consult. Likewise the card catalog of the average university or general library may be unsatisfactory, for it must be understood that in any search beyond the purely obvious, indexes and ordinary card catalogs are not the simple tools most people believe them to be.[3] They may contain the reference to an article or a book but the relevancy of the heading under which the reference is entered may be apparent only after the desired information has been located in some other way. Recently biographical data regarding a well-known scientist were found accidentally in the autobiography of one of his former students. No catalog or index previously consulted had revealed that source.

When it comes to the problem of looking up a name, subject, or compound, if it is readily found, all is well. If not, a host of questions arise, such as correct spelling, various scientific names for the same substance, trade names versus scientific names, different words for the same idea, language variations (azote—nitrogen), general terms versus specific, new and old headings ("Kinetics" for "Rate of reaction"), unusual and unfamiliar terms ("escharotics" for "nitric acid"), and many others.

The technic of searching varies with the problem in hand. In any case the knack of saving time is essential. It involves a knowledge of the various bibliographical tools and their individual peculiarities. For example, a fundamental difference between the subject indexes of *Chemical Abstracts* and *Chemisches Zentralblatt* is that the latter has a classified index while the former uses subject entries. Keys to other reference books have all sorts of idiosyncracies, some due to the fact that people unfamiliar with indexing principles are responsible for their construction.

Another factor equally important is the method. A trained searcher arranges the source materials according to his notion of their pertinence. He first examines every item in the primary group, reserving a portion of his available time for the other divisions. The exact amount of this residual time depends upon his application of the Law of Diminishing Returns. Obviously the greatest danger for a novice is the possibility of misjudging the relevancy of an item. In any event, a search must be conducted so that it terminates with a definite feeling that nothing essential has escaped examination.

One search method too frequently ignored is that of association. The chemicals, apparatus, conditions, operator and even geographical location are united in the production of any result. Consequently, when one seeks a procedure for the analysis or purification of a substance, good sources should be articles reporting the determination of some physical property such as the freezing point. Information about low temperature technic, in general, would naturally be expected in articles from the various cryoscopic laboratories.

The tendency of a beginner is to accept any statement found in print without carefully checking the original report, evaluating it and determining whether the figures are reasonable and the conclusions justified by the data. It is so easy to overlook typographical errors, to generalize from insufficient evidence, even to misinterpret the results, that laboratory verification is desirable in cases sufficiently important.

The ideas and data in books are frozen assets while they remain on the shelves unknown to the needy technician. Due to the sheer bulk of chemical literature the task of finding a specific item of information is frequently beyond the ability of an untrained investigator. This situation should not be a cause for alarm, but a frank admission that narrow specialization is in accord with the trend of the times. One is no longer a chemist, even a physical chemist, but—more specifically—a colloid chemist. The colloid chemist may be fairly well acquainted with the literature of his own field, by the "contact process"; but for anything beyond, he is well advised to seek aid from an equally specialized library technologist. Through their combined efforts library research can effectively catalyze laboratory research.

[3] *Cf.* CRANE, *Ind. Eng. Chem.*, **14**, 901 (1922).

RUBBER THE REMARKABLE

"No other material is like vulcanized rubber. It stretches and then it snaps back. Compressed, it springs again to its original size and shape. In this becushioned age of ours these uncommon properties have become enormously important.

"This curious material is as versatile in form as it is distinctive in physical properties. It comes to us hard and stiff in the fountain pen barrel; soft and pliable in the delicate sheets of pure gum the dentist uses; tough and springy to heel our shoes. There are rubbers made as porous as a first-grade Key West sponge; crumbly rubber for the artists' erasers; liquid rubbers to mix with paints or to coat underseas cables and electrical wiring.

"Rubber the Remarkable, the material of over three thousand good uses—to be without rubber is a dismaying thought, even a little frightening, since nothing else will quite do."

Rationed Rubber and What to Do About It
Williams Haynes and Ernst A. Hauser

Ceramics and Industrial Minerals in the War Effort

HENRY G. FISK *Armour Research Foundation, Chicago, Illinois*

THE PRESENT age has been truly called the age of metals, and the importance of metals in modern industry and in the tools of war cannot be minimized. However, it is seldom realized that ceramics and the non-metal industries play an extremely strategic role in the war effort as well as in our peacetime economy. According to the Bureau of Mines,[1] in 1940 the value of our non-metals production exclusive of fuels ran $824,600,000 which was approximately one-half of that of the metals. Without the refractories which form the linings of our blast furnaces and open-hearth furnaces, production of our iron and steel would immediately stop. The same is true in regard to the production of other ferrous metals such as electric furnace steels, as well as most of our non-ferrous metals.

Although an increasingly large portion of our chemical industries is concerned with plastics and products derived from strictly organic raw materials, the bulk of our heavy chemical industries still obtain the major portion of their raw materials from "things that come out of the ground." Inorganic chemicals such as, for example, lime and sulfuric acid, our cheapest base and acid, respectively, are derived from mined or quarried raw materials.

In addition to these most important roles which ceramics and industrial minerals play in the production of our metals and chemicals, ceramic products are assuming greater importance in the present emergency as substitutes for certain metals of which the war has created an acute shortage.

GLASS

One of the more important of these ceramic products is glass, which is playing a dual role in the war effort. On the one hand glass is a strategic product, when used in various combat instruments, both offensive and defensive, in the form of precision lenses or prisms in binoculars, range finders, telescopes, airplane landing lights, search lights and various other optical instruments.

The less direct uses of glass are not so obvious, but they are important. For example, glass is finding greater use in the construction and container fields, in each of which it is releasing steel, zinc, and tin for more important purposes.

Glass as fine fibers forms glass wool, an ideal lightweight fire-proof and vermin-proof insulating material. In this form it may be employed in bulk or fabricated into bolts and rolls. For marine insulation, bats having a bulk density of four pounds per cubic foot are employed. It is reported that the saving in weight on a modern battleship through the use of fiber glass insulation is about sixty tons.

Fiber glass is also woven into fabrics with many unique uses. Among these is that in the electrical field where fiber glass tapes are used as insulation in the windings of motors, generators, transformers, and various electrical appliances. Another is the use of woven glass fiber inserts as filters in the flexible tubes employed in giving blood plasma transfusions.

A new and interesting development of glass is its use for sound-recording discs in which the glass disc is coated with a lacquer which takes the actual sound impression. It is said that this type of disc is quite satisfactory in the place of aluminum.

One of the more recent and technically important developments in glass is that of tempered glass, which is now used for such things as doors in railroad cars and store fronts, glass sinks and drain-boards and other applications. By tempered glass is meant glass which has been subjected to a rapid heating followed by an instantaneous cooling. Fundamentally there is nothing new about hardening glass by such a method, as "Prince Rupert drops" with their extremely hard surface have been known for years. The new developments lie rather along the line of improved technic for heating and chilling the surface of the glass. The cooling is usually done by blasts of air or quenching in oil, which rapidly cool the inner and outer surfaces simultaneously. Tempered glass is reported to have a strength approximately four to five times that of ordinary glass of the same thickness and has the further advantage that when it does break it tends to disintegrate into a great number of extremely small particles and not into the larger, jagged particles into which ordinary glass breaks.

In developing a substitute for the tinned containers which have become an American institution, the glass industry has come forward with glass containers. These containers have the obvious advantage that the contents of the "can" may be readily observed on the retailer's shelf by the housewife. In this connection the question of the effect of light on the vitamin-

[1] Minerals Yearbook Review of 1940.

retaining qualities of glass containers is of interest to all. Recently this subject was investigated[2] and the conclusions of a rather extensive study are that the effect of heat is far more pronounced than the effect of light; that changes in vitamin C content attributed to light are really insignificant and occur only under prolonged storage conditions.

PORCELAIN

Porcelain products are essential in a number of military appliances and processes as well as for the better known uses of chemical porcelain. For example, "steatite," the new type of electrical porcelain in which is incorporated a large percentage of talc or steatite, finds wide application as an insulating material in radio tubes and other communication equipment. One airplane radio set, for example, uses 360 steatite parts.

One company is making steatite porcelain ferrules which are employed in a stud welding process to replace bolts which fasten wooden decking in ship construction. The porcelain ferrule acts as a shield for the arc and keeps oxygen and nitrogen from the molten metal.

We hear a great deal about 100-octane gasoline these days. How many people, however, realize that the engines in our airplanes—pursuit ships to bombers—depend upon ceramics in the form of the essential spark plug for their functioning? Great strides in the development of aviation-type spark plugs were made during the last war, and since that time the automotive industry has continued to improve the spark plug until today the performance of this necessary part of the engine has been brought up to that of the fuels used and the engine itself.

PORCELAIN ENAMEL

The durable coating which is bonded through fusion to metal surfaces has recently found a place as a substitute for the more critical nickel, chromium, and copper fittings used in plumbing. Also, enameled kitchen ware is finding acceptance in the place of aluminum and stainless steel, thus releasing larger quantities of these critical metals for defense purposes. Other uses for enameled metals are found in certain types of construction; for example, partitions for showers and exterior finishes of buildings.

ABRASIVES

Grinding is an extremely vital process in the production of modern metal parts. Castings and hardened bearings or wearing surfaces range all the way from huge castings used in the moving parts of the modern battleship or tank to the precision pins and bearings of the watch-like mechanisms which control the path and detonation of torpedos or bombs. Abrasives, either in grain form or bonded in the shape of grinding or cutting wheels and discs, are speeding up metal removing and shaping operations in many machined parts at one stage or another. The commonest types of modern abrasives are fused alumina and silicon carbide, both products of the electric furnace. Supplementing these are boron carbide, the hardest known synthetic product, and industrial diamonds. The latter are still not produced synthetically, and constitute the hardest known substance. Synthetic sapphires, a pure form of fused alumina, are used in great numbers for precision bearings in all manner of delicate instruments. The development of methods of piercing and cupping these jewels for use makes an interesting story. Another field in which industrial diamonds are employed is the wire drawing industry, in which the size of wire is reduced by cold drawing through a diamond die.

PORTLAND CEMENT

One of our large industries from the standpoint of tonnage is the cement industry which in 1939 produced 24,440,000 tons (130,000,000 bbls.) of cement. This is due to the widespread demand for this essential ingredient of concrete for various types of construction such as buildings, roads, and airports. Also, cement is necessary for the construction of immense concrete dams for the generation of hydroelectric power so vital to the needs of the nation. The purely military demands on portland cement for naval bases, gun implacements, and drydocks are greatly increasing the need for cement at the present time. An interesting trend in cement manufacture is the recent tendency away from the extremely fine-ground cement which was so widely advocated and used during the last few years. It is now rather generally realized that the large amount of power used in grinding cement to the fineness formerly recommended for high early strength can be more effectively expended in other directions, especially since a more durable concrete generally results when a somewhat less finely ground cement is used. The saving of wear on tube-mill linings and steel balls by producing the more coarsely ground product is also an important consideration in the conservation of steel.

REFRACTORIES

Brief mention was made of the place of basic refractories in the manufacture of steel by the basic open-hearth process. The blast furnace in which is produced the pig iron directly used for steel is lined with high quality clay refractories. Refractories are no less essential, as was pointed out, in the production of electric furnace steels and non-ferrous metals such as copper and zinc.

The boilers of our naval vessels as well as the steam boilers of power generating plants which use fuels as their source of energy are also lined with refractories for retention of heat and protection of their metal shells.

Kyanite, a naturally occurring aluminum silicate, was formerly employed for special refractory applications. The only entirely suitable grade of kyanite for this purpose was formerly imported from India. With

[2] *Ceramic Industries*, **39**, 38 (1942).

this source of supply cut off, the refractory industry is investigating topaz from which the fluorine has been volatilized, together with a portion of the silica, by a high temperature calcination. The composition of kyanite is represented by the formula Al_2SiO_5 and that of topaz is $(AlF)_2SiO_4$. Tests on calcined topaz are very favorable. An extensive deposit of topaz in South Carolina[3] gives promise of supplanting the Indian kyanite in refractories. This topaz is not of the gem variety, and in fact has an appearance not unlike certain forms of common quartzite.

CLAYS

Clays constitute a large and varied class of mineral raw materials. Mention was made of the use of clay refractories for lining blast furnaces. For this and other purposes clays of high quality are required, but not necessarily white burning clays. Porcelain manufacture and other uses where color of the finished product is an important consideration require white burning clays, most of which were formerly imported from England. Now, however, domestic clays are meeting almost all the requirements of industry, although English clays are still entering this country.

The consumption of china clays, or white burning kaolins, is distributed about as follows in normal times: 59 per cent to the paper industry, 11 per cent to the rubber industry, 11 per cent in the manufacture of pottery and tile, 9 per cent in the manufacture of refractories, 5 per cent in the manufacture of cement; and other industries, including the paint, linoleum, and oilcloth industries, approximately 5 per cent. The significance of these figures lies in the fact that the strictly ceramic industries—namely the pottery, tile and refractory industries—consumed only 20 per cent of the china clay which was used in 1940. Thus it is apparent that this type of clay is a vital material in many industries.

Bleaching or decolorizing clays known as "fuller's earth" find application in clarifying vegetable and mineral oils. Bentonite, a clay that often exhibits unusual swelling properties, finds special use as a bond clay. A large portion of the bentonite produced is employed as a binder in molding sands for metal foundries. Bentonite is sometimes used as a sealer to prevent water flow or percolation in engineering works where water leakage must be stopped. Bentonite is also used as a detergent, and a plasticizing or bonding agent in conjunction with other clays.

LIMESTONE

Limestone produced constitutes approximately 75 per cent of all stone quarried or mined in the United States, and in 1935 was in excess of 139,000,000 tons. Of this quantity, the manufacturing and chemical industries consumed over 25,000,000 tons in the same year, of which approximately three-fourths, or 17,000,000 tons, was employed as metallurgical or flux stone. As fluxing limestone or lime it is used in the manufacture of pig iron, steel, and non-ferrous metals. As a base it combines with acid impurities, such as silicon, sulfur, and phosphorus, to form the fusible slag by which these and other impurities are removed. Lime, the product of calcination of limestone, is the cheapest and most widely employed base in the chemical industry. Acetylene, used for steel cutting and welding, is manufactured from calcium carbide, which in turn is produced by the reaction of lime and coke at 2000°C. in the electric furnace. Acetylene is also employed for synthetic rubber production.

MINERALS

Quartz of a certain kind is said to be one of our strategic minerals.[4] Clear quartz is cut into plates less than one millimeter thick and used to control radio frequency. These plates are cut at definite angles with respect to the axes of the crystal and are ground with parallel surfaces. The thickness of the quartz plate governs the frequency, and such control is necessary for every radio in use on aircraft, tanks, and submarines. The most important source of "piezoelectric" quartz, the type suitable for this, is Brazil, although Madagascar and the United States have produced some of proper quality.

Attempts to make synthetic quartz suitable for commercial use have not yet been successful. Thus, all radio communications depend upon naturally occurring quartz crystals for their functioning, since no satisfactory substitute has been found. Tourmaline, another naturally occurring mineral, has piezoelectric properties similar to those of quartz, but plates of this mineral must be cut so thin in order to be useful that they lack mechanical strength to withstand normal usage. Rochelle salt, potassium sodium tartrate, which can be grown into large crystals in the laboratory, may be used for this purpose under some conditions, but crystals of this salt are subject to deterioration, and their mechanical properties are not equal to those of quartz.

Common salt, in the form of the mineral halite, ranks next to lime in importance as a heavy chemical. In 1939 over 10,000,000 tons of salt were produced in the United States. The bulk of this salt enters chemical industries. Sulfur, another mineral and chemical raw material, is mined in the natural state.

Other strategic minerals perhaps better known because of their important and essential uses in ferrous alloys are pyrolusite and psilomelene, the most important minerals of manganese ores, and scheelite and wolframite in which tungsten occurs.

[3] *Bull. Am. Ceramic Soc.*, **21**, 135–39 (1942).

[4] *Mining and Met.*, **23**, 374(1942).

The 8000 tons of steel which used to go into novelties and souvenirs would make 160,000 0.50 calibre machine guns.

Simple Projection Manometer For Lecture Demonstrations

JOHN W. MOORE[1] and CARL M. FURGASON[1] *University of Texas, Austin, Texas*

THE MANOMETER described below can be placed in the slide carrier of a standard lantern slide projector, so that lecture demonstrations involving pressure changes may be advantageously shown to large groups.

The projection manometer is assembled from 18 inches of 6-mm. glass tubing and 1/4-inch plywood. Different dimensions might, of course, be required to fit the particular projector with which the manometer is to be used. The complete unit, as shown in Figure 1,

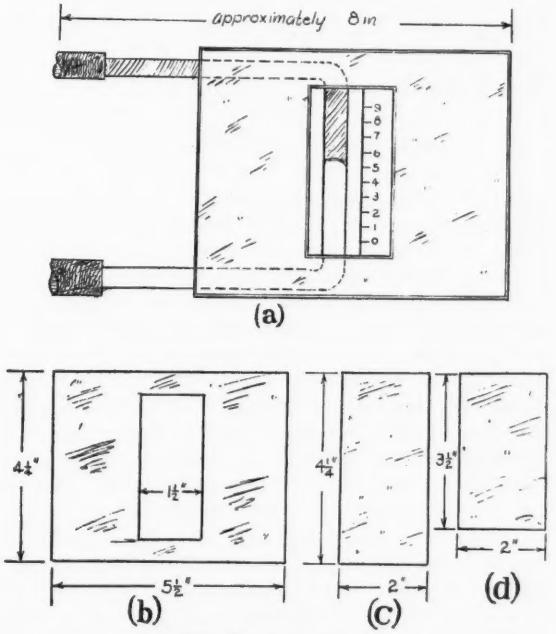


Figure 1.

CONSTRUCTION DETAILS OF PROJECTION MANOMETER

consists of the tubing held between two outside plates (Figure 1*b*) which are separated by spacer blocks (Figures 1*c*, 1*d*). The plates and blocks may be fastened together by brads or small screws. A six-inch transparent ruler may be used for the scale, fastened midway between the outer plates. The system being observed can be connected to either end of the manometer tube, as shown in Figure 2*a* or as in Figure 2*b*.

[1] Present address: Tennessee Valley Authority, Wilson Dam, Alabama.

If the range in pressure or liquid level is larger than the projected portion of the manometer tube, a flask fitted with a funnel may be connected between the

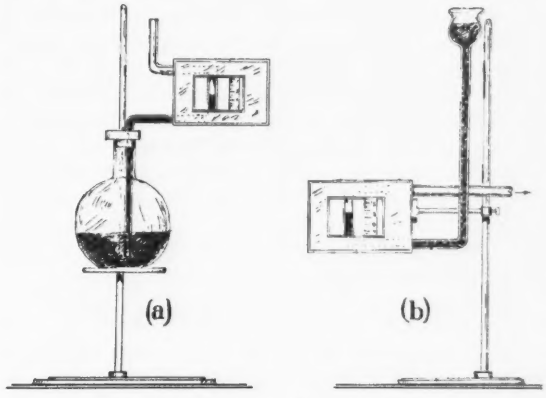


Figure 2.

ALTERNATE METHODS OF CONNECTING MANOMETER TO SYSTEM

manometer and the system under observation (Figure 3). The demonstrator may adjust the liquid level in the projection manometer to any desired point on the scale by manipulating the stopcock. For example, should the meniscus disappear from view on the screen, the stopcock is opened and the meniscus restored to its original position without appreciably disturbing the system.

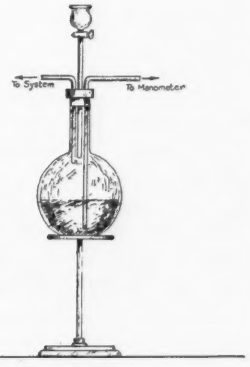


Figure 3.

APPARATUS FOR READJUSTING LEVEL IN MANOMETER

Acknowledgment

The authors wish to express their appreciation to Dr. W. A. Felsing for his assistance in preparing this manuscript, and to Mr. Arthur Patureau for making the drawings.

High Polymers and New Rules

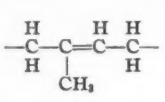
S. WEINER *Paul-Lewis Laboratories, Inc., Milwaukee, Wisconsin*

OUR system of chemistry began in the hands of Boyle, Dalton, and Lavoisier with gases and with compounds of low molecular weight. Thus it happened that the criteria of a compound developed along these lines: a compound consists of particles, called molecules, which are all alike but different from the molecules of other compounds. It can be isolated and purified, that is, its molecules can be separated in bulk from foreign molecules. It has a definite composition; this indeed has long been the definition of a compound. It has a fixed definite chemical equivalence that determines the weight relations in which it reacts with other pure substances. This chemical equivalence (or equivalent weight) is one of its important constants. It has a definite molecular weight, which is also an important constant. Only in a few cases involving tautomerism (*e. g.*, acid-base indicators), association (*e. g.*, liquid water), or dissociation (*e. g.*, N_2O_4), do we apply the term *compound* to a substance disobeying any of the above rules.

HIGH POLYMER CHEMISTRY

The plastic industry and the use of x-ray diffraction have produced substances and facts to which the usual ideas of a compound are inapplicable. Chemists in industry are accustomed now to speak of rubber, polystyrene, polybenzyl, and other high polymers as if they were compounds. Chemists in general have long been speaking of cellulose, starch, and albumin as if these too were definite compounds. There is arising now a new branch of chemistry, the field of the high polymers, in which the orthodox rules fail. Gradually and unconsciously, chemists are using the word "compound" with a new set of meanings. The "compounds" of protein or plastic chemistry are not at all compounds in the older sense.

Today, the most generally accepted theory of the structure of the high polymers pictures them as composed of many long-chain molecules, often branching and interlocking. In bakelite and many other plastics the chains are so frequently branched and interconnected that they form a three-dimensional network, thus giving to the product the rigidity of a solid. The chains are not all of the same length, of course, and so in the usual terms we would say that the material is a mixture, since its molecules are not of one kind. Such molecules are built up by the repetition of a certain unit, such as

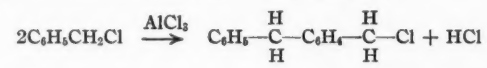


in rubber or

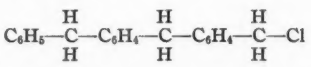
in polystyrene, so in a sense the mixture consists of a homologous series of compounds in which the repeating unit is other than CH_2.

STOICHIOMETRIC LAWS FAIL

High polymers do not always obey the Law of Definite Proportions. There is often a gradual change in elementary composition as the proportion of the larger chains increases Polybenzyl is made by the condensation of benzyl chloride. The dimer has about half the chlorine content of the monomer:



Similarly, the trimer



and the higher polymers contain progressively less chlorine. Again, the ratio of oxygen to carbon progressively diminishes in any sample of cellulose or protein as the degree of polymerization increases.

Hence, the high polymers are characterized by a certain indefiniteness. No two batches of pure cellulose or of starch have been exactly alike in all their properties. No two samples of pure keratin have been identical in composition. Polystyrene can be separated by extraction or precipitation into fractions of identical composition but different properties and different molecular weights (*1*). Nevertheless, the varieties and fractions of any given high polymer have a certain sameness and semi-uniformity that marks them as variable samples of a given type-substance. All samples of cellulose are celluloses and all varieties of starch are starches. Moreover, no cellulose can be mistaken for a starch nor any starch for a cellulose, though their elementary composition be the same. Composition seems not to be of crucial importance here.

Nor can we say that such indefinite substances should be called mixtures of homologs, for often their component particles are joined together by the same covalent bonds that bind atoms into a single molecule of a compound. In bakelite and the glyptal resins these bonds extend throughout the mass of the body, so that each specimen is a huge covalent molecule. Indeed, Fuoss refers to the diamond as the ideal case of a completely covalent cross-bonded polymer, implying it to be the end-type of high organic polymers (*2*). Once more we find the concepts and classifications useful in

low-molecular chemistry to be merely confusing in the high molecular field. Each high polymer is now considered to be a single compound, just as hydrogen is still considered a single element, despite the isotopes composing it.

Polymers are not altogether amenable to the Law of Multiple Proportions. The addition of another methylene group or other structural unit to the molecule of a high polymer causes either no change in the ratio of the weights of two or more elements or so slight a change that no definite multiples of a common factor can be observed. Had chemistry begun with the high polymers instead of with the gases and simple salts, these stoichiometric laws would never have been discovered. This disappearance of the Law of Multiple Proportions at high molecular weights is analogous to the Correspondence Principle in quantum mechanics. According to the latter principle, at high quantum numbers a unit change of quantum number is comparatively so small that the radiation laws of quantum chemistry become identical with the radiation laws of classical electrodynamics and the radiating atom or molecule acts as a continuous emitter rather than as a quantized emitter.

Just as the composition of a high polymer need not be definite, so its equivalent weight need not be constant. The weight of a given reagent that will combine with one gram of a given polymer can vary continuously in a certain range as the degree of polymerization changes. Indeed, the value of the reacting weight of a high polymer in a suitable reaction is often used as a method, the "end group" method, for determining the degree of polymerization. Thus, Kraemer and Van Natta (*3*) determined the average chain length in polymerized ω-hydroxy decanoic acid by titrating the acid groups at the ends of the long molecules. Again, Staudinger and Lohmann (*4*) measured the polymerization of a polyethylene oxide by determining the acetyl groups it reacted with to form the diacetate. The equivalent weight of a high polymer gradually rises as the reactive bonds in the polymer are consumed in the polymerizing.

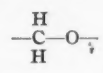
MOLECULAR WEIGHTS OF SECONDARY IMPORTANCE

Hence, too, the molecular weight has an entirely different significance in polymer chemistry from that which it has in low molecular chemistry. It is not a constant specific to the substance, with a fundamental bearing on its chemical structure. Rather, the "molecular weight" of a high polymer is often an average of the molecular weights of the molecules composing the polymer. These molecules may vary in size over a broad range and, with one exception, any experimentally determined molecular weight will be merely a weighted average. That exception is in the use of the ultracentrifuge; it indicates the variation in molecular weights and it separates polydisperse suspensions into their fractions. But even the term "average molecular weight" is ambiguous. A given sample may have at least two "average molecular weights": a number-average molecular weight, related to the osmotic pressure, the freezing point depression, and the equivalent reacting weight, and a weight-average molecular weight, related to the viscosity and the settling in an ultracentrifuge (*5*). The particular average to be used in any case depends on the property being studied.

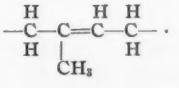
In the high polymers the molecular weight is not a molecular constant but a parameter subject to control. In the plastic industries the essential step is the raising of the average molecular weight by promoting the polymerization, often by heat and pressure. In the cellulose industry we generally try to maintain the molecular weight high; cellulose of low molecular weight is referred to as "degraded" and has poor tensile strength. On the other hand, in the manufacture of viscose rayon, the cellulose xanthate dispersion is allowed to "ripen" for several days while the long chains decompose and the molecular weight drops; the dispersion is spun through orifices into the coagulating fluid at the moment when the molecular weight is low enough so that the dispersion is not too viscous for the spinning but before the molecular weight has fallen to a figure too low to permit formation of a high tensile strength fiber (*6*). But whatever the molecular weight of a cellulose sample, we consider the sample to be a cellulose. The molecular weight is here not a unique mark of identity. There is a difference between acetic acid (molecular weight, 60) and propionic acid (molecular weight, 74), but a change of one glucose ring in a cellulose chain of 2000 such rings causes negligible difference in the physical properties and none in the chemical.

STRUCTURE AND PERIODICITY

The emphasis that in low molecular chemistry is placed on composition and molecular weight is placed on structure and periodicity in the high polymers. The individualizing characteristic of a high polymer is the structural unit, an atom group out of the repetition of which the substance is built. In cellulose it is the glucose anhydride ring arranged in pairs as in cellobiose: in the polyoxymethylenes it is



and in rubber it is



In the proteins a succession of several amino acid anhydrides constitutes the chain. These units are joined together by strong bonds, most probably identical with ordinary homopolar valence. The repetition of the units may be along a linear chain or there may be frequent branchings of the chain so that the unit repeats itself in two or three dimensions.

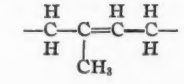
The structural unit is analogous to an atom in orthodox low molecular chemistry, and the analog of the molecule is the micelle or crystallite. In certain polymers, such as the cellulose and protein fibers, there

are small submicroscopic regions characterized by an orderly arrangement of the parallel chains of structural units. These orderly regions, called *crystallites* or sometimes *micellae*, have been regarded by some as units of the fiber structure and also as units existing independently in solution when the fiber is dissolved or dispersed. The frequency, distribution, and structure of these crystallites determine many of the physical and industrial properties of the polymers in the solid state. There is disagreement, however, as to whether they exist as such in solution.

As if in compensation for the lost stoichiometric laws, there arises among the proteins a new atomism. In 1928 Mark and Meyer (*7*) decided from X-ray evidence that the chains in fibroin, the protein of natural silk, were composed of alanine and glycine residues in alternation. This can be symbolized as GAGAGA . . . However, a more complete study later showed the repeating unit to be not GA but GAGX, where X is an amino acid other than glycine and alanine. Bergmann and Niemann (*8*) suggested the sequence to be GAGT, GAGAr, GAGY, GAGY, where T represents tyrosine, Ar stands for arginine, and Y represents amino acids other than those mentioned.

Waldschmidt-Leitz (*9*) reported the herring protein, clupein, to be MArAr, MArAr, MArAr, PArAr, MArAr, where P is proline and M is one or other of the monoamino mono-carboxylic amino acids. Bergmann and Niemann amass data to support their contention that the number of amino acid groups in a protein molecule is always either 288 or a simple multiple thereof and that the amino acids are distributed along it in a definite periodicity. All this suggests a new order of atomism: The amino acid anhydrides are the "atoms" in the protein molecule, the periodic repetition being analogous to the crystal lattice in simpler compounds. But in these cases the lattice is *within* the molecule.

The industrial properties and X-ray diffraction pattern of true synthetic (polyprene) rubber are influenced by the regularity with which the CH_3 groups are arranged along the chain of



units.

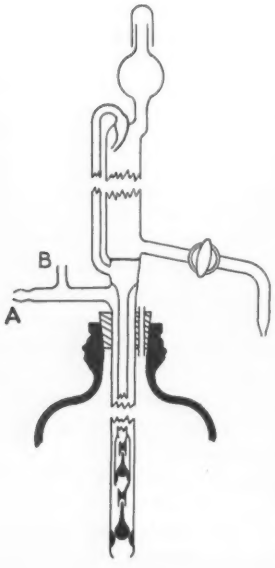
LITERATURE CITED

(1) CAROTHERS, *Chem. Rev.*, **8**, 395 (1931).
(2) FUOSS, J. CHEM. EDUC., **19**, 235 (1942).
(3) KRAEMER AND VAN NATTA, *J. Phys. Chem.*, **36**, 3175 (1932).
(4) STAUDINGER AND LOHMANN, *Ber.*, **68**, 2313 (1935).
(5) KRAEMER AND LANSING, *J. Phys. Chem.*, **39**, 165 (1935).
(6) FOX, *J. Soc. Chem. Ind.*, **49**, 84T (1930).
(7) MEYER AND MARK, *Ber.*, **61**, 1932 (1928).
(8) BERGMANN AND NIEMANN, *J. Biol. Chem.*, **118**, 301 (1937); **122**, 577 (1938).
(9) WALDSCHMIDT-LEITZ AND KOFRANYI, *Z. physiol. Chem.*, **236**, 181 (1935).

AN AUTOMATIC BURET FOR DISPENSING VOLATILE REAGENTS

JOHN W. MURRAY

Thomasville Stone and Lime Co., Thomasville, Pennsylvania



AUTOMATIC burets for dispensing reagents, which operate by air pressure pumped into the top of the bottle, have been on the market for several years. When this type of buret is used with volatile reagents such as ammonium hydroxide and hydrochloric acid, large amounts of fumes are blown out into the room when the pressure is released, especially if the bottle is nearly empty. To overcome this disadvantage, the type of automatic buret described below was designed.

The reagent is pumped into the buret by the double-valved glass pump actuated by alternate air pressure and suction applied to the liquid between the inner and outer tubes by a rubber bulb attached at *A*. The hole *B* is closed by a finger, or other device, after expelling sufficient air to permit sucking the liquid between the tubes to a level slightly below *A*. Pumping is facilitated by making the volume of liquid displaced at each compression large by a suitable selection of tubing diameters and by keeping the inlet to the inner tube as low as possible. Excessive constriction at the valves, inlet holes, and delivery jet should be avoided. Operation of the automatic leveling feature of the buret depends on the imperfection of the upper valve, so it should not be ground to fit perfectly.

The volume of air expelled into the room is restricted to a part of the volume of the rubber bulb plus the volume of the liquid pumped into the buret. Fumes may be partially removed from this air by a trap containing a suitable absorbing material. Three of these burets have been operating satisfactorily in the author's laboratory for about a year.

Courses in Advanced Analytical Chemistry

I. Texts for Courses in Applied or Technical Analysis

PHILIP J. ELVING, *Purdue University, Lafayette, Indiana*

IT IS THE belief of many teachers of analytical chemistry that, after the usual course in elementary quantitative chemical analysis covering the fundamentals of gravimetric and titrimetric technic, the student of analytical chemistry should be introduced to the procedures and methods actually used in industry, research, and control testing. This applies especially to the various courses in applied or technical analysis, including courses in water analysis, alloy and steel or metallurgical analysis, and fuel analysis. Many students who enter industry after receiving a bachelor's degree are assigned to analytical work in which they use the methods devised and published by some official or standard-setting body such as the U. S. Bureau of Mines or the American Society for Testing Materials. Most chemists who enter research have occasion, more or less frequently, to use standardized procedures in connection with their work. An organic chemist, who has prepared a new compound which has possibilities as a solvent, would probably determine the flash and fire points, viscosity, and other technical constants. All of these individuals, teachers, students, research chemists, would have benefited from an introduction to the type of procedure given in an official method which usually is very different from the procedures with which they become acquainted in the elementary textbooks in quantitative analysis.

In connection with the present extensive array of chemistry courses in the national war training program, the use of standard and official procedures is especially advantageous from the viewpoints of expediency, standardized training, and pedagogy.

Many instructors of analytical chemistry are apparently unaware of the material available for use in courses which deal with the technical examination of materials. It is the purpose of this article to call to their attention the availability, at nominal cost, of a large number of pamphlets and books dealing with the analysis or testing of many classes of materials which are published by various governmental departments and bureaus, as well as by different associations and societies which function as standard-setting bodies. Some of the latter groups sell publications intended for use by students at reductions up to fifty per cent of the list price. The Government Printing Office gives a discount of twenty per cent on any order of one hundred or more government publications. For the cost of the average textbook the student can purchase a large number of booklets, pamphlets, and books which will be of great value to him in his professional career.

The use of such material as textbooks and laboratory manuals has much to commend it from the teaching standpoint. Students are enthusiastic about using this material, which they very much prefer to the usual type of textbook. The work of the laboratory and the discussion in the class are made much more real to them. There is revealed to the students the importance in actual life of that which they are studying in the classroom. The latter is of great educational and psychological advantage. The result is a better performance of work, since the students see the advantage to themselves of learning the course material properly. Another result is the improvement of the students' laboratory technic, since the need of attention to small details is stressed in standardized procedures. The use of these publications might well be combined with the use of a textbook to form a well-rounded course.

The one big disadvantage in the use of the material here advocated is the lack of discussion, in most standard procedures, of the underlying theoretical basis of the method used. However, this deficiency can be readily remedied by the instructor's lectures or proper assignments to library books. In the author's courses the class coöperates to buy several copies of one or more textbooks or reference works to supplement the library facilities. In certain fields, the need for discussion of the procedures used is filled by the excellent monographs of the American Society for Testing Materials which interpret the results obtained in the examination of various classes of materials.

During the past three years the various courses in technical analysis taught at Purdue have used official or standard procedures in many fields, including gas and fuel analysis, water analysis, and microscopy. The use of such procedures has been most successful from all angles.

There is listed in the following sections a selected and annotated bibliography of such publications. The annotation is limited to a brief characterization of the item, summarizing its contents and indicating its applicability. The publications described can be secured from the publisher whose name is given in parentheses at the end of each reference, except in the case of government publications, where the name of the issuing bureau or the descriptive series title of the publication is given. All government publications should be bought from the Superintendent of Documents, Government Printing Office, Washington, D. C. Any government publication for which no charge is made can be obtained from the issuing department. For convenience in ordering from the Government Printing Office, the order numbers used by the Office are given as the last item in the reference. The special price charged for publications intended for student

use is inserted in parentheses after the list price. To secure this special price, which is usually one-half of the list price, the American Society for Testing Materials and the American Public Health Association require that ten or more copies be bought at the same time.

The author would like to express his thanks to Professor M. G. Mellon of Purdue University for his help and suggestions.

AGRICULTURAL ANALYSIS

Methods of Analysis of the Association of Official Agricultural Chemists. 5th ed. 1940. 769 pp. $5.00 (Association of Official Agricultural Chemists). This authoritative reference is eminently suited for use as a laboratory manual in courses in agricultural analysis, agricultural chemistry, or food analysis, since the methods given in it are those which will be used in future years by the students. Due to the wide variety of classes of substances for which methods are included, it could well be used in courses in general technical analysis or in pharmaceutical analysis.

ROBINSON. *Method and Procedure of Soil Analysis Used in the Division of Chemistry and Physics.* Rev. 1939. 23 pp. 5¢ (Agriculture Department, Circular 139) A 1.4/2: 139. A useful laboratory guide for the topic indicated in its title.

SNYDER. *Methods for Determining Hydrogen-ion Concentration of Soils.* Rev. 1935. 48 pp. 5¢ (Agriculture Department Circular 56) A 1.4/2: 56. A useful reference or text for a more advanced course in agricultural analysis.

MERKLE. *Soil Testing: Operation, Interpretation, and Application.* 1940. 34 pp. (The Pennsylvania State College Agricultural Experiment Station, Bulletin 398.)

MORGAN. *Soil Testing Methods.* 1939. 16 pp. (Connecticut Agricultural Station, Circular 127.)

THORNTON, CONNER, AND FROSER. *The Use of Rapid Chemical Tests on Soils and Plants as Aids in Determining Fertilizer Needs.* 1939. 16 pp. (Purdue University Agricultural Experiment Station, Circular 204 (rev.).) This and the two preceding publications are representative of similar publications by most state experiment stations on simple methods for testing soils. Pamphlets of this type would be useful not only in courses in agricultural analysis, but also in courses in general technical analysis.

COAL ANALYSIS

POPE, revised by SNYDER. *Directions for Sampling Coal for Shipment or Delivery.* 1933. 8 pp. 5¢ (Mines Bureau, Technical Paper 133) I 28.7: 133. The procedure for sampling coal is given, including the collection of the gross sample and the reduction to laboratory size. The large folding plate illustrates by means of 34 small sketches the steps in reducing a 1000-pound sample to a 2.5-pound sample by the long pile-alternate shovel and quartering procedures.

A.S.T.M. Standards on Coal and Coke. 1940. 123 pp. $1.25 (65¢) (A.S.T.M.). This collection of the A.S.T.M. specifications and methods of sampling, testing and analysis of coal and coke is suitable for both laboratory and class work in coal analysis. It includes the Bureau of Mines plate on the reduction of the gross sample of coal to the laboratory sample.

STANTON, FIELDNER, AND SELVIG. *Methods of Analyzing Coal and Coke.* Edition of 1938. 59 pp. 15¢ (Mines Bureau, Technical Paper 8) I 28.7: 8. This pamphlet fills all requirements for a laboratory guide for the proximate and ultimate analysis of coal and coke. The sections on the fusibility and analysis of coal ash are especially useful for students. The only noteworthy omission is that of the peroxide method for sulfur.

Symposium on Significance of Tests of Coal and Coke. 1937. 126 pp. $1.00 (50¢) (A.S.T.M.). This is a collection of six papers on the interpretation of the laboratory tests and analytical determinations made on coal and coke and the connection between the results of these tests and the uses to which coal is put. It is recommended for class study to supplement laboratory work on coal analysis.

FIELDNER AND SELVIG. *Notes on Sampling and Analysis of Coal.* 1938. 48 pp. 10¢ (Mines Bureau, Technical Bulletin 586) I 28.7: 586. The theoretical and practical points involved in both the proximate and ultimate analysis of coal are covered. Two-thirds of the pamphlet is devoted to an excellent discussion of the interpretation of the results obtained in analyzing coal. The sections on calorific value and sampling are especially noteworthy. An excellent text for lecture or recitation.

Symposium on Industrial Fuels. 1936. 70 pp. 75¢ (40¢) (A.S.T.M.). The four papers in this booklet present a comprehensive survey of coal and coke, industrial fuel oils, manufactured gas, and liquefied petroleum gas. Included are the availability, types, tests made and their significance, utilization, and economical aspects. The material is useful reading for background and orientation in the field of fuels and fuel testing.

GAS ANALYSIS

KREISINGER AND OVITZ. *Sampling and Analyzing Flue Gases.* 1915. 70 pp. 15¢ (Mines Bureau, Bulletin 97) I 28.3: 97. Although rather old, the booklet contains a valuable discussion, copiously illustrated, of the technic of obtaining flue gas samples. The procedure described is for one using the conventional 3 pipet flue gas Orsat. Some 10 pages are devoted to a discussion of the use of flue gas analysis in promoting boiler room efficiency.

FORBES AND GROVE. *Mine Gases and Methods for Their Detection.* Rev. 1937. 82 pp. 30¢ (Mines Bureau, Miners' Circular 33) I 28.6: 33. Material for special experiments in gas analysis could be obtained from this monograph. It can also be used to illustrate the many special types of detectors available for methane, carbon monoxide, hydrogen sulfide, and other mine gases.

YANT AND BERGER. *Sampling Mine Gases and Use of Bureau of Mines Portable Orsat Apparatus in Their Analysis.* Rev. 1936. 90 pp. 10¢ (Mines Bureau, Miners' Circular 34) I 28.6: 34. The publication includes a comprehensive discussion of the problem of sampling gases (28 pp.) and a discussion of the preparation, care, and use of a typical Orsat apparatus for gas analysis. The Orsat discussed consists of three absorption pipets and one combustion pipet. The analytical procedures given can be used in analyzing any ordinary flue or fuel gas with any of the conventional three pipet flue gas models or Orsat apparatus of three to four absorption and one combustion pipet. The booklet can be used for both class discussion and laboratory.

Burrell Manual for Gas Analysts. 3rd ed. 59 pp. Free (Burrell Technical Supply Co.). With the exception of the last few pages this pamphlet is devoted to a usable discussion of the theory and practice of gas analysis with Orsat type apparatus, supplemented by methods for calorific value, hydrogen sulfide, and specific gravity. There is sufficient material for a short survey, laboratory and class, of the field of gas analysis.

MATUSZAK. *Fisher Gas Analysis Manual.* Rev. ed. 64 pp. Free (Fisher Scientific Co.). Two-thirds of this publication are devoted to a practical discussion of the assembling and use of apparatus of the Orsat type, with special emphasis on the unitized type of apparatus sold by the publisher of the booklet. The latter is essential in courses using the apparatus in question and would be of help in using other types of Orsat apparatus.

SEGELER, editor. *Fuel Flue Gases.* 1942. 198 pp. $2.50 ($1.50) (American Gas Association). This attractive volume is largely concerned with the application and interpretation of gas analyses and tests. After an introductory section (14 pp.) on the pertinent physical chemistry of gases, the chemical analysis and physical testing of gases together with the application of the data obtained are discussed. This is followed by a consideration, including special analytical methods, of the possible constituents of fuel gases. Gas distribution systems, furnace atmospheres for many purposes, industrial atmospheres, and uses of gases as chemical raw materials are discussed with emphasis on the aid supplied by gas analysis in maintaining maximum efficiency. This book would be excellent as a text in courses in gas analysis to supplement the laboratory procedures given in the Bureau of Mines publications.

SMITH. *Utilization of Natural Gas for Chemical Products.* 1940. 8 pp. Free (Mines Bureau, Information Circular 7108). The composition and general uses of natural gas and the four chief methods by which it is converted into other products are well presented in the form of charts. This paper would be interesting supplementary reading to work in gas analysis.

METALLURGICAL ANALYSIS

A.S.T.M. Methods of Chemical Analysis of Metals. 1939. 256 pp. $2.00, paper; $2.50, cloth ($1.00, $1.25) (A.S.T.M.). All of the A.S.T.M. methods for the chemical analysis of ferrous and non-ferrous metals are given, including procedures for the analysis of steels and various types of irons and ferro-alloys, brass and bronze, bearing metals and solders, aluminum and its alloys, copper, lead, nickel, and zinc. Also included are procedures for the quantitative spectrometric analysis of zinc and lead alloys by the standard series method. This book is recommended as a laboratory manual for courses in metallurgical analysis but should be supplemented by lectures or reading on the chemistry of the methods used.

CHURCHILL AND BRIDGES. *Chemical Analysis of Aluminum.* 2nd ed. 1941. 120 pp. 50¢ (Aluminum Company of America). This spiral-bound, convenient of size booklet ably presents the methods used in analyzing metallic aluminum and aluminum alloys, and would be useful as a text in a course in metallurgical analysis. The use of this booklet would serve to introduce the students to an excellent example of the work being done by certain industrial laboratories in developing procedures which cover all of a particular field of analysis.

Standard Methods for the Sampling and Analyzing of Aluminum and Certain Aluminum Alloys. 2nd ed. 1939. 31 pp. Free (Aluminum Research Institute). The contents are indicated by the title.

SCHERRER. *Determination and Separation of Arsenic, Antimony, and Tin.* 1936. 7 pp. 5¢ (Bureau of Standards, Research Paper 871) C 13.22/a: 871.

SCHERRER. *Determination of Arsenic, Antimony, and Tin in Lead-, Tin-, and Copper-base Alloys.* 1938. 10 pp. 5¢ (Bureau of Standards, Research Paper 1116) C 13.22/a: 1116. This and the preceding pamphlet furnish a very successful procedure for determining the three elements indicated in all types of copper-base and bearing-metal alloys. These determinations would fit very well into a study of metallurgical analysis. The rather uncommon use made in this procedure of fractional distillation as a means of separating metallic elements will increase the student's perspective on inorganic analytical separations.

Simple Methods of Analyzing Plating Solutions. 6th ed. 1941. 42 pp. Free (Hanson-Van Winkle-Munning Co.). A number of titrimetric procedures useful in the control of electroplating have been gathered together in this pamphlet which might be used in metallurgical analysis or electrochemistry.

SLOMIN. *Rapid Quantitative Electrolytic Methods of Analysis.* 4th ed. 1942. 40 pp. $1.00 (E. H. Sargent and Co.). These methods, which are intended to be used with the apparatus for rapid electro-deposition manufactured by the publisher, can be used for the rapid determination of many of the elements found in non-ferrous alloys with any type of rotating electrode.

MICROSCOPY

BAUSCH. *The Use and Care of the Microscope.* 1939. 31 pp. Free (Bausch and Lomb Optical Co.). The manipulation of the microscope is stressed in this pamphlet, which also includes a brief discussion of the theory of the microscope. This publication would be of great value in introducing the student to the microscope and its manipulation.

The Microscope. 1935. 62 pp. Free (Spencer Lens Co.). This brief monograph covers the construction, use, and care of the microscope. A useful elementary treatment of microscope optics is included. This booklet would fulfil the same purpose as the preceding one.

FRY. *Petrographic Methods for Soil Laboratories.* 1933. 96 pp. 15¢ (Agriculture Department, Technical Bulletin 344) A 1.36: 344. This booklet is an excellent reference for the study of chemical microscopy. Although special laboratory experiments are not included, the various types of measurements and observations that can be made with a polarizing microscope are well described. The theory involved in refractive index determination and the use of polarized light is well presented. The latter part of the book is devoted to a detailed account of the application of microscopic methods to a number of problems associated with soil and agricultural chemistry.

LARSEN AND BERMAN. *Microscopic Determination of Nonopaque Minerals.* 2nd ed. 1934. 266 pp. 25¢ (Geological Survey, Bulletin 848) I 19.3: 848. This publication should be available in all laboratories in which work in chemical microscopy is done. After a short section on methods for determining the refractive indices and other optical properties of minerals and other inorganic crystals, comprehensive tables are given for identifying minerals from their optical properties.

SHORT. *Microscopic Determination of the Ore Minerals.* 2nd ed. 1940. 314 pp. $1.00 (Geological Survey, Bulletin 914) I 19.3: 914. This book could be used as the basis of a course covering its title or it could be used in a regular course in chemical microscopy. Besides a thorough treatment of the preparation of polished sections and of the determination of the physical properties and etch properties of minerals, there is an excellent treatment of microchemical inorganic qualitative analysis by microscopic methods (125 pp.). The latter is illustrated by a number of splendid color plates of crystalline precipitates.

Photomicrography. 13th ed. 1935. 122 pp. $1.00 (Eastman Kodak Co.). This book would be extremely useful in any course in chemical microscopy which included photomicrography. The only point of fault is the omission of a discussion of photography in polarized light.

Basic Photography. 1941. 342 pp. 35¢ (War Dept., Technical Manual 1-219) W 1.35: 1-219. This manual is an excellent reference for the photographic side of the work in photomicrography.

LOFTON. *Photomicrography of Paper Fibers.* 1922. 22 pp. 5¢ (Bureau of Standards, Technologic Paper 217) C 13.8: 217. A useful reference for photomicrography and for the study of fibers and pulps.

TESTING OF PETROLEUM PRODUCTS

Federal Standard Stock Catalog: Lubricants and Liquid Fuels, General Specifications (Methods for Sampling and Testing) 176 pp. 15¢ T 58.10/3: VV-L-791a. This booklet is a "best buy" in the field of laboratory manuals, covering the government tests made on the various types of petroleum products. The procedures given are essentially those of the A.S.T.M. The pamphlet contains an adequate number of illustrations and photographs of apparatus. It also contains a number of tests that have not been standardized by the A.S.T.M. It is recommended for use in the courses on the testing of petroleum products.

A.S.T.M. Standards on Petroleum Products and Lubricants. 1940. 360 pp. $2.00 ($1.00) (A.S.T.M.). Included in this collection are all of the A.S.T.M. official and tentative methods for the testing of petroleum products. Also included are specifications for various types of oils and definitions of terms used. This is an excellent laboratory manual, but the booklet embodying the government specifications is much less expensive while including substantially the same material.

SYMONS, editor. *The Waverly Handbook.* 9th ed. 1937. 902 pp. $2.00 (Waverly Oil Works). The petroleum industry in all its phases is discussed in this handy little book. Since over a hundred pages are devoted to the A.S.T.M. procedures for testing petroleum products, this book could be used as both text and laboratory manual in covering the testing of petroleum products, especially if class work on petroleum refining and utilization were to be included.

WILHELM, editor. *Tag Manual for Inspectors of Petroleum.* 26th ed. 1942. 159 pp. $1.00 (C. J. Tagliabue Mfg. Co.). This well-known book provides succinct summaries of the various A.S.T.M. procedures which are used in testing petroleum products, including a number of methods which are not included in

the A.S.T.M. or government specifications. The tables and illustrations are excellent. It is an excellent laboratory manual, especially if procedures are desired which omit the thermometer and other apparatus specifications found in standardized procedures. It would be very suitable for an adult education course.

U.O.P. Laboratory Test Methods for Petroleum and Its Products. Rev. ed. 1940. $3.00 (Universal Oil Products Co.). A collection of methods, used in the laboratories of a large petroleum company, intended to supplement the A.S.T.M. methods and including many other commonly used methods. A number of recently developed analytical methods which promise to be useful are included, as well as a section on special methods of gas analysis which would be very useful in a course dealing with gas analysis. This publication would be useful in any course in fuel testing, especially if extra experiments are desired covering less common phases of the field.

The Significance of Tests of Petroleum Products. 1937. 76 pp. $1.00 (50¢) (A.S.T.M.). A very useful discussion of the methods used in testing petroleum products, including the interpretation of the results obtained, is found in this reference. Since the type of tests made on petroleum products can be interpreted only in the light of the past performance of materials of that type having similar properties, this monograph is essential as a supplement to any laboratory work on the testing of petroleum products.

Evaluation of Petroleum Products. 1940. 52 pp. 75¢ (40¢) (A.S.T.M.). The six papers included in this monograph discuss the current status of the tests made on petroleum products and suggest the direction in which these tests might be modified to be more serviceable. The material is more technical than that presented in the monograph on *The Significance of Tests of Petroleum Products;* however, it could be used for supplementary reading and discussion, where a more advanced treatment of the subject is desired.

Lubricants. 1937. 89 pp. $1.25 (75¢) (A.S.T.M.). This symposium report, which is suitable for background reading in a course on the testing of petroleum products, contains four extensive papers, of which the one on the selection of a motor oil from the consumer's viewpoint is of most interest. It probably does not contain a sufficient amount of usable material to justify every student purchasing a copy, but library copies should be available.

WARD. *Review of the Literature on the Construction, Testing, and Operation of Laboratory Fractionating Columns.* 1939. 36 pp. 10¢ (Mines Bureau, Technical Paper 600) I 28.7: 600. This would provide interesting and valuable class material for a course on physico-chemical methods of analysis or in an extended course on the testing of petroleum products.

DETERMINATION OF pH

Modern pH and Chlorine Control. 5th ed. 1940. 80 pp. Free (W. A. Taylor and Co.). Over half the material in this reference is devoted to an excellent discussion of the determination of pH, with emphasis on the factors which influence the behavior of indicators in various types of solutions. This is supplemented by an interesting account (15 pp.) of the application of pH control in over thirty different fields. The last quarter of the booklet is devoted to apparatus for the colorimetric determination of pH and the colorimetric analysis of water, manufactured by the publisher. This booklet might be used in a course which included the colorimetric determination of pH.

The ABC of pH Control. 10th ed. 1934. 64 pp. Free (LaMotte Chemical Products Co.). About one-third of the text is devoted to a discussion of pH and its determination. The remainder of the material covers the use of the publisher's apparatus in the colorimetric determination of pH, chlorine, and other technically important quantities or substances and in water analysis and other fields where colorimetric or titrimetric technics can be used.

Apparatus for Hydrogen-Ion Concentration Measurements in Laboratory and Plant. 1939. 44 pp. Free (Leeds and Northrup Co., Catalog EN-96). Laboratory or class work involving the potentiometric determination of pH can be adequately performed using this catalog and the directions supplied with the instrument as guides.

ROCK AND MINERAL ANALYSIS

HILLEBRAND. *The Analysis of Silicate and Carbonate Rocks.* 1919. 285 pp. 25¢ (Geological Survey, Bulletin 700) I 19.3: 700. The reputation of this book in the field of rock analysis is so well established that it is unnecessary further to recommend it, except to remark that it is probably the outstanding value, in the view of its price, in all of chemical literature. In addition to serving as a laboratory guide in rock analysis, it is a very valuable reference work for the analytical literature up to its date of publication.

HOFFMAN AND LUNDELL. *Analysis of Phosphate Rock.* 1938. 20 pp. 5¢ (Bureau of Standards, Research Paper 1095) C 13.22/a: 1095. The procedures used by the Bureau of Standards in analyzing standard samples of phosphate rock are described together with a brief discussion of the methods. The pamphlet would be usable either in rock or metallurgical analysis.

CLARKE. *Data of Geochemistry.* 5th ed. 1924. 841 pp. $1.00. (Geological Survey, Bulletin 770) I 19.3: 770. This well-known treatise on geochemistry with its stress on analytical results is well worth the attention of any one engaged in rock analysis. A copy of it should be available in any laboratory devoted to rock analysis and selected portions of it might well be assigned as background reading. In addition to the comprehensive discussion of the formation, alteration, and composition of rocks, a hundred pages are devoted to metallic ores, a hundred and fifty pages to natural waters, and fifty pages to natural hydrocarbons and coal.

CLARKE, editor. *Analyses of Rocks and Minerals from Laboratory of the United States Geological Survey. 1880–1908.* 1910. 323 pp. 25¢ (Geological Survey, Bulletin 419) I 19.3: 419; *1914–1936.* 1937. 134 pp. 15¢ (Geological Survey, Bulletin 878) I 19.3: 878. These two compilations might be made available to students engaged in rock and mineral analysis in order that they might realize the importance of the subject, comprehend the typical composition of various classes of natural materials, and appreciate the precision possible as regards summation of the analytical results.

SPECTROMETRIC ANALYSIS

MEGGERS AND SCRIBNER. *Index to the Literature on Spectrochemical Analysis, 1920–1939.* 2nd ed. 1941. 94 pp. $1.00 (50¢) (A.S.T.M.). A thorough list of publications on chemical analysis by emission spectroscopy during the past two decades. The 1446 references are arranged by year with the items published each year arranged alphabetically according to author's name. Under each paper reference is made to some published abstract of it, usually in *Chemical Abstracts.* There is a complete subject index, useful as a reference for courses in spectrometric analysis.

Tools of Analytical Chemistry and Spectrographic Analysis. 1941. 56 pp. 50¢ (25¢) (A.S.T.M.). The material on spectrometric analysis would make excellent background reading for any student of spectroscopy since the factors influencing the accuracy of emission spectrometric analyses and the interpretation of these results to the engineer and layman are emphasized. The papers on the tools of analytical chemistry would be good reading for courses in advanced and technical analysis.

Symposium on Spectrographic Analysis. 1935. 51 pp. 65¢ (35¢) (A.S.T.M.). This collection of six papers might be used as supplementary reading in a course in chemical spectroscopy, the papers on the influence of non-homogeneous samples in steel analysis and on the quantitative analysis of non-ferrous alloys being especially helpful.

HOLMES, SCANLAN, AND PETERSON. *The Visual Spectrophotometry of Dyes.* 1932. 43 pp. 5¢ (Agriculture Department, Technical Bulletin 310) A 1.36: 310. Although somewhat out of date, this material might be of some use for class discussion.

WATER ANALYSIS

Standard Methods for the Examination of Water and Sewage. 8th ed. 1936. 323 pp. $2.50 ($2.25) (American Public Health

Association). This definitive work is the most suitable laboratory manual for courses in water analysis. Its only defects are the omissions of a discussion of the chemistry of the methods used and of the interpretation of water analysis.

COLLINS. *Notes on Practical Water Analysis.* 1927. 32 pp. 10¢ (Geological Survey, Water-supply Paper 596-H) I 19.13: 596-H. A concise account of the methods commonly used in determining the mineral constituents of water intended for industrial use. Besides the usual determinations there is included a systematic procedure for the analysis of the residue obtained on evaporation. There is a short but good section on the graphical representation of analytical results.

Water Analysis. 2nd ed. 1941. 93 pp. Free (Solvay Technical and Engineering Service, Bulletin No. 11). A collection of methods suitable for the mineral analysis of the water supplies used for municipal and various industrial purposes. There is a very useful section on the preparation of indicators, reagents, and standard solutions. It could be used as a laboratory manual.

Water Handbook. 1942. 64 pp. 50¢ (W. H. and L. D. Betz). This handy large-sized booklet is divided into two sections, one giving procedures for the chemical analysis of water and the other dealing with the theory of each test made and the application to plant control of the information secured. The booklet would be useful in a short treatment of water analysis where the A.P.H.A. book could not be used, while the section on interpretation of the tests could be used to supplement the latter work.

THERIAULT. *Detailed Instructions for Performance of Dissolved Oxygen and Biochemical Oxygen Demand Tests.* 1931. 34 pp. 10¢ (Public Health Service, Supp. 90 to Public Health Reports) T 27.6/2: 90. This is a useful supplement to the A.P.H.A. *Standard Methods* in carrying out the important B.O.D. tests.

Determining Steam Purity. 1941. 80 pp. 60¢ (30¢) (A.S.T.M.). This collection of papers on the sampling of steam and boiler water, conductivity apparatus, and other aspects of the problem cited could be used for supplementary reading on this important aspect of the field of applied water analysis.

HOOVER. *Water Supply and Treatment.* 2nd ed. 1936. 145 pp. $1.00 (National Lime Association, Bulletin 211). The various methods of water purification and softening for industrial and sanitary purposes are well discussed in this volume. The numerous illustrations and diagrams are very helpful in developing the subject. The book could be used for supplementary reading or as a class text in a course in water analysis.

Alkalies and Chlorine in the Treatment of Municipal and Industrial Water. 1940. 84 pp. Free (Solvay Technical and Engineering Service, Bulletin No. 8). A practical discussion of the various methods of water purification and softening together with a discussion of the steps in municipal and industrial water purification. The tables of illustrative data are especially helpful. This bulletin would provide excellent class material for a course in water analysis.

Questions and Answers on Boiler Feed-water Conditioning. 1936. 121 pp. 20¢ (Mines Bureau, Question and Answer Handbook 3) I 28.48: 3. A series of questions and answers on the causes and prevention of boiler troubles including some on the analysis of water preliminary to softening and on the chemicals used in softening. A handy booklet for class work in a course in water analysis.

COLLINS, LAMAR, AND LOHR. *Industrial Utility of Public Water Supplies in the United States, 1932.* 1934. 135 pp. 15¢ (Geological Survey, Water-supply Paper 658) I 19.13: 658. The first part (37 pp.) of this pamphlet is devoted to a discussion of the constituents found in water and of the treatment of water supplies; the remainder consists of tables of analyses of public water supplies all over the United States. The former material would be valuable if read in the early part of the course on water analysis.

MISCELLANEOUS

Abstracts for Special Reagents. Free (Eastman Kodak Co.). The Eastman Kodak Co. has available a large number of one-page mimeographed abstracts covering the use of a large number of specific and selective organic and inorganic reagents in various analytical determinations. These procedures could be used in many courses in technical analysis. A list of the special reagents for which procedures are available can be obtained from the company.

A.S.T.M. Standards on Cement. 1940. 116 pp. $1.00 (50¢) (A.S.T.M.). About one-fourth of this book is devoted to methods for the chemical analysis of cement which material could be used not only in courses in general analysis but also in a course in rock analysis. In addition, some of the material on physical testing could probably be used.

Federal Standard Stock Catalog: Cements, Hydraulic, General Specifications (Methods for Sampling, Inspection, and Testing) 1941. 10¢ T 58.10/3: SS-C-158a. This little booklet contains methods for the chemical analysis (7 pp.) and physical testing of cement. The material could be well used in a course in general technical analysis.

Symposium on Color—Its Specification and Use in Evaluating the Appearance of Materials. 1941. 80 pp. $1.00 (50¢) (A.S.T.M.). The interesting topic of color and its measurement in precise terms might well be introduced into a course in advanced analytical chemistry, or in courses in fields like paint or textile testing where color is important. This book would serve as an excellent introduction to the subject.

MONROE AND TIFFANY. *Physical Testing of Explosives at Bureau of Mines Explosives Experiment Station, Bruceton, Pa.* 1931. 148 pp. 35¢ (Mines Bureau, Bulletin 346) C 22.3: 346. This book could be used for class work in a course dealing with explosives. Some of the methods described could be carried out in the average university laboratory.

TAYLOR AND RINKENBACH. *Analysis of Detonating and Priming Mixtures.* 1922. 33 pp. 5¢ (Mines Bureau, Technical Paper 282) I 28.7: 282. While this pamphlet can be used both as a laboratory manual and for class discussion, the instructor should exercise due care in any laboratory work involving explosives. The procedures used should be checked against more recent publications on the subject.

A.S.T.M. Standards on Paint, Varnish, Lacquer, and Related Materials. 1941. 347 pp. $2.00 ($1.00) (A.S.T.M.). Material for laboratory work on the physical and chemical examination of paints and allied materials, both in the raw and finished states, can be selected from this compilation of specifications and standardized tests.

Federal Standard Stock Catalog: Paint, Varnish, Lacquer, and Related Materials. General Specifications (Methods for Sampling and Testing) 1941. 40 pp. 10¢ T 58.10/3: TT-P-141. This little booklet might find use in a course in general technical analysis.

GARDNER. *Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors.* 9th ed. 1939. 578 pp. $12.75 (Institute of Paint and Varnish Research). This is the definitive reference for the examination of paints and allied materials. Unfortunately, its high cost prohibits its use except as a reference work in all but specialized courses in paint testing.

A.S.T.M. Standards on Textile Materials. 1940. 355 pp. $2.00 ($1.00) (A.S.T.M.). The material given in this collection of specifications and methods can be used in any course in textile or general technical analysis. Some of the methods described could also be used in courses in chemical microscopy.

Early wooden statuary was preserved by rubbing olive, cedar, or juniper oil over the surface, or by pouring these oils into numerous small holes bored into the wood.

Natural and Synthetic Rubbers

HARRY L. FISHER *U. S. Industrial Chemicals, Inc., Stamford, Connecticut*

PART I—NATURAL RUBBER

INTRODUCTION

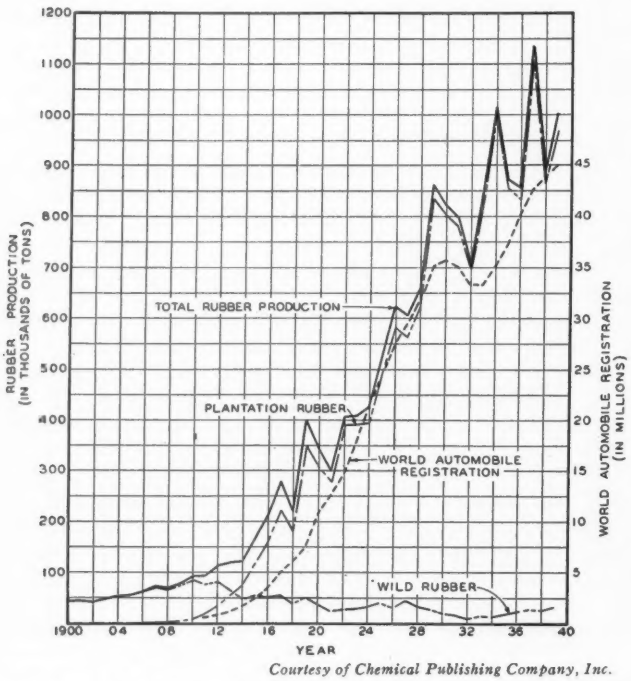
THE unique properties of rubber have made it an indispensable article of commerce. Its resilience, elasticity, and impermeability to water brought it into use even before Columbus discovered America. Later in the early 1800's, crude rubber from South and Central America was being imported into Europe and the United States for the manufacture of raincoats (mackintoshes), play balls, overshoes, bottles, life preservers, and thread for elastic fabrics. In 1834, as much as 540 long tons were received in this country. However, difficulties inherent in the crude rubber itself caused much trouble since rubber becomes hard and unyielding in the cold of winter and soft and sticky in the high temperatures of summer, and in air and sunlight it deteriorates to a resinous mass of useless material. The interest in rubber was great but it could not withstand such natural hindrances.

Then came Charles Goodyear with his indomitable pioneer spirit and his dogged determination to make rubber more lasting and therefore more useful. For several years he experimented while he encountered business reverses and he and his family suffered great poverty, but he was finally rewarded when in 1839 he made the observation of the "change" which later became known as vulcanization. Sulfur and heat properly applied laid the foundation, and sulfur and heat still form the foundation of the rubber industry.

Rubber received its name from the fact that, in the words of Joseph Priestley, it was "excellently adapted to the purpose of wiping from paper the marks of a black lead-pencil." The word, however, is used very loosely, since it is the name not only of the natural raw material but also of the vulcanized products made therefrom. At present it has come to mean also any material with rubber-like properties.

SOURCES AND PRODUCTION OF NATURAL RUBBER

Natural rubber occurs as a suspension of tiny particles in the white milk-like fluid known as latex which is found in the leaves, bark, and roots of a wide variety of trees, shrubs, and vines. Our common milkweed, *Asclepias syriaca*, and the old household rubber plant, *Ficus elastica*, are typical examples of latex-bearing plants. However, practically all the natural rubber of commerce comes from a tree, *Hevea brasiliensis*, which grows in the Amazon Valley, and since 1876 has been cultivated on the great plantations that are scattered throughout the tropical Far East and certain portions of tropical Asia, Africa, and the Americas. These plantations cover approximately 9,000,000 acres—an area, if all put together, of about the size of the combined states of Massachusetts, Connecticut, and Rhode Island—and produce around 1,000,000 long tons annually. The corresponding production of rubber from trees growing wild is only about 20,000 long tons. In normal times about half of the total rubber produced is imported into the United States. The price is around 20 cents a pound. The important relationship of the growth of the rubber plantations to the growth of the automobile industry is shown in the accompanying chart.



Courtesy of Chemical Publishing Company, Inc.

COMPARISON OF RUBBER PRODUCTION AND WORLD AUTOMOBILE REGISTRATION

Commercial latex is obtained only from the bark of the tree, and this is done by a system known as tapping. A slanting cut is made with a U-shaped tool and a channel formed in it to allow the latex which oozes out to flow to the lower end where it is caught in a cup. Every other day a new slice or shaving is removed from the channel by the same instrument and a new lot of latex collected. A good tree yields about 2 ounces at each tapping. The latex consists of about 35 per cent of rubber and therefore one

tree produces about 6 pounds of dry rubber a year. Since the average tire contains approximately 10 pounds of rubber the annual output of two trees is required for its manufacture.

The latex is collected and then coagulated with dilute acetic acid. Latex resembles cow's milk, but latex coagulum consists chiefly of a hydrocarbon while the milk coagulum consists chiefly of protein—like cottage cheese. The rubber coagulum is passed through corrugated steel rolls to squeeze out the serum, which is washed away by running water. The particles of rubber adhere to one another and now form a sheet. Natural rubber comes on the market generally in three forms: pale crepe, a washed and dried product with an appetizing odor; smoked sheet, which is dried in smoke as its name implies and smells like smoked ham; and amber blankets, a reworked product of scrap material and the output of individual farms run by natives.

Latex can be preserved by the addition of a small proportion of ammonia, and it can be concentrated by means of a centrifuge or by creaming. In these forms it is shipped for use in the manufacture of rubber goods directly from latex.

MILLING CRUDE RUBBER

Crude rubber is very tough and ordinarily must be worked on a mill before the necessary compounding ingredients can be mixed into it. Milling rubber causes it to become soft and plastic, and then all kinds of ingredients—powders, abrasives, rubber substitute, oils, waxes—can be mixed in. In all cases, except with solvents, rubber remains the outer phase; *i. e.*, the rubber surrounds the suspended matter, rather than vice versa. Milling of rubber is accompanied by the action of a very small amount of oxygen, so small, in fact, that it is difficult to determine it. In the complete absence of oxygen, no "breakdown" is noticeable. The first sight of broken-down rubber makes one wonder how it can ever be converted into useful products, but vulcanization under the proper conditions performs this apparent miracle. Much breakdown is required for some purposes, especially for the extruding of tubes, but generally the breakdown is not made any greater than necessary for the object in mind, since the greater the breakdown, the lower are the final physical properties. In the manufacture of articles from latex in which the rubber is not broken down, the physical properties are very high.

RESULTS OF RESEARCH

Knowledge of the chemistry and physics of rubber was meager until after the turn of the century. The increase in the use of rubber for tires and tubes gave the impetus for a deeper study of the properties of rubber. Also, the development at the same time of colloid chemistry was a strong factor in the further study of rubber, since it, too, is a colloid. It is of interest that a great deal of the research work on rubber has been done in the laboratories of the rubber and chemical industries. The discoveries of organic accelerators, of antioxidants, and of the abrasion resistance of compounds reinforced with carbon black, have been of the utmost importance, and these have all been discovered in industrial laboratories.

Courtesy of The Firestone Tire and Rubber Company

A NATIVE TAPPING A PLANTATION RUBBER TREE

PROTECTED RUBBER IS PERMANENT

If rubber is kept away from air and light it does not deteriorate. Rubber products submerged in water last a long time. In certain German lignite mines the workmen are familiar with rubbery fibers known as "monkey hairs." These are now known to consist of fossil vulcanized rubber and are the remains of rubber originally in the twigs of a type of rubber-bearing shrub now found only in Africa. The surrounding lignite contains a small proportion of sulfur and, in the course of thousands of years, the sulfur migrated and caused the formation of prehistoric vulcanizates.

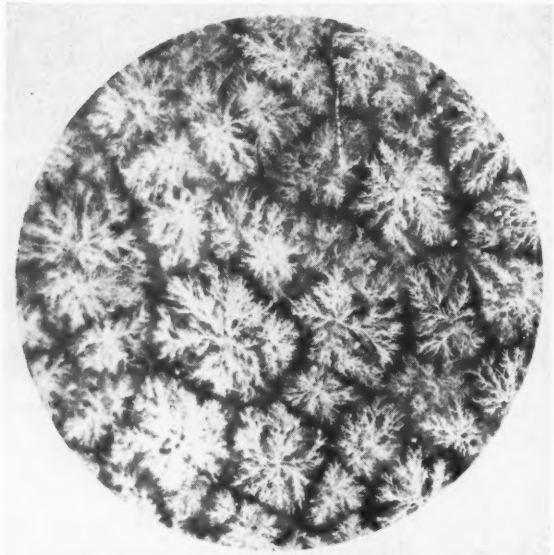
VULCANIZATION

Although the use of sulfur as a vulcanizing agent was discovered over a hundred years ago, it is still practically the only vulcanizing agent used. Other agents are known, but their use is very limited. Therefore vulcanization of crude rubber as discussed in this paper means vulcanization with sulfur.

Vulcanization produces definite changes in the rubber. These changes can be defined and frequently measured; yet no good theoretical explanation of vulcanization has been made.

Vulcanization enhances the elastic properties of crude rubber and extends them over a wider range of temperatures. Vulcanized rubber is strong, elastic and non-sticky at temperatures even above the boiling point of water, where raw rubber is sticky and weak like putty. At 40° below zero, where raw rubber is hard and non-elastic, vulcanized rubber is still elastic and usable; for example, in airplane tires. Furthermore, vulcanization of rubber decreases its solubility

in common solvents and, what is most important, decreases its "plastic flow" and its permanent "set." Another way of stating the differences between crude and vulcanized rubber is that crude rubber is elastic and thermoplastic, whereas vulcanized rubber is even more elastic but non-thermoplastic. Properly vulcanized rubber when stretched returns to approxi-



Courtesy of Bell Telephone Laboratories

DENDRITIC SULFUR

Dendritic sulfur in masticated pale crepe after standing two days

mately its original position, and the same piece can be stretched time and again with the same results.

During vulcanization it is known that the sulfur combines chemically with the rubber hydrocarbon, but this chemical combination does not explain all that takes place. Furthermore, the rate of chemical combination of sulfur has never been explained fully, since the curve of the rate of addition versus time is a straight line function, and the law of mass action seems to have no effect. The proportion of chemically combined sulfur to give soft vulcanized rubber may vary from approximately 0.5 to 5 per cent. Rubber with 32 per cent of sulfur chemically combined has all its double bonds saturated, and such a vulcanizate is hard rubber or ebonite. The types of compounding, the use of different accelerators, and different temperatures, all affect the type of final product. Generally, the practical precedes the theoretical, and this statement is well borne out in the field of rubber.

ACCELERATORS

Accelerators, as the name implies, speed up vulcanization. However, not only do they reduce the time of vulcanization and thus allow more rapid turnover of molding equipment, but they also give products that have many desirable properties not obtainable by sulfur alone. The proportions used are very low, only 0.5–1.5 parts to 100 parts of rubber. Some of them allow vulcanization to take place at lower temperatures than those ordinarily used, even at room temperature. By the use of these ultra-accelerators the proportion of sulfur can be reduced to as low as 0.5 part to 100 of rubber, and this reduction is often an advantage, since low-sulfur stocks usually have high resilience and show very good resistance to aging and the action of heat.

Certain ultra-accelerators, the thiuram disulfides, are of special interest, since they vulcanize rubber without the addition of any elemental sulfur. An example is tetramethylthiuram disulfide,

$$(CH_3)_2NCS{\cdot}SS{\cdot}CSN(CH_3)_2.$$

The most important accelerator is mercaptobenzothiazole ("Captax"). Others are dibenzthiazyl disulfide ("Altax"), diphenylguanidine ("DPG"), and condensation products of aniline and aliphatic aldehydes.

COMPOUNDING RUBBER

Rubber is practically always used in the compounded vulcanized state. Unvulcanized rubber is used only in cements, as crepe rubber soles for shoes, and in a few other minor instances. To make rubber of commercial value, it must be mixed with the proper compounding ingredients and then vulcanized. The choice of the proper ingredients and the proper combination and proportions of ingredients makes possible the infinite

Courtesy of Bell Telephone Laboratories

RHOMBIC SULFUR

Dendritic sulfur transformed to rhombic sulfur in masticated pale crepe after standing for 14 days

variety of uses of rubber products. Besides sulfur, accelerators and antioxidants, many other substances are incorporated into rubber to give the required properties. Carbon black is used, as already mentioned, as the chief reinforcing agent for resistance to abrasion. It also helps to give high tensile strength, high resistance to tear, and stiffness. The semi-

reinforcing blacks also give high tensile strength, good resistance to tear, and fair resistance to abrasion, along with softness and pliability. Zinc oxide, magnesium carbonate, blanc fixe, and certain clays act somewhat like the semi-reinforcing blacks, although tensile strength and resistance to tear are generally lower when some of them, especially clays, are used. Inert fillers such as whiting, infusorial earth, some clays, barytes, and slate flour are used to give body or weight, when high tensile strength and resistance to abrasion are not necessary. Oils, waxes, tars, and mineral rubbers (gilsonite, etc.) are used as softening agents.

TRANSPARENT RUBBER

A good grade of crude rubber is transparent, but ordinary vulcanized rubber is not. By using a low proportion of sulfur and by proper choice of accelerators to avoid the later formation of crystalline masses, and by using a basic magnesium carbonate with a refractive index close to that of rubber, it is possible to produce sheets of well-vulcanized rubber that are permanently transparent.

MOLDING

Practically all rubber articles are molded. For molding it is necessary to build up rubber compounds with the proper ingredients, in order that the final product will be of the desired quality and dimensions. The work of the compounder, who plans the compound for a definite purpose, is very important. It is he who outlines what must be mixed into rubber in order that such small objects as plungers for hypodermic needles, and such large objects as great airplane tires, will be properly vulcanized and do the work required of them. A mistake is costly, for once the object is vulcanized it cannot be taken apart and done over again; in other words, vulcanized rubber has never been devulcanized.

OPTIMUM CURE

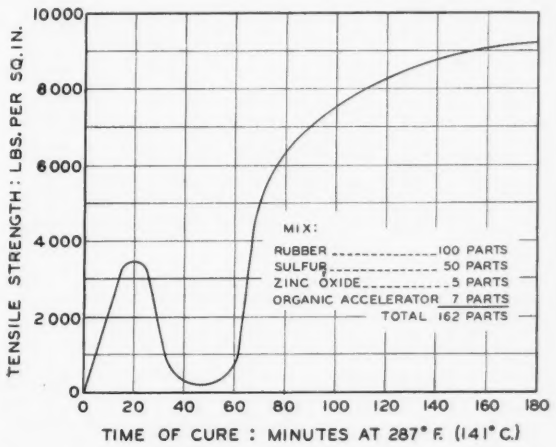
Properly vulcanized rubber, that is, rubber which has the "best" properties, is said to have the "optimum cure." Such a cure is difficult to define, but it ordinarily has the highest tensile strength obtainable with the compound being studied, has good elongation, low permanent set, and good tear resistance. An "undercured" stock, obtained by heating for a shorter time or at a lower temperature, has a low tensile strength, a high elongation, is more soluble than the stock with the optimum cure, shows poor aging, and in general is "sleazy." An "overcured" stock, obtained by a longer time of heating or at a higher temperature, may also have a low tensile strength, is "short" (that is, has low stretch), usually tears easily, and generally is rather hard and harsh. As a rule, the stock with the optimum cure gives the best service, including good aging.

TABLE-TOP CURES

For many years compounds were generally cured at 141° to 147°C. (40 to 50 lbs. per sq. in. steam pressure). However, compounds cured at lower temperatures usually have better physical properties than those cured at higher temperatures. Certain accelerators can be used at lower temperatures, about 130°C. (25 lbs. per sq. in. steam pressure), and fortunately these accelerators give sustained properties, even though the stock is cured for a rather long period of time. In other words, they have a tendency to prevent overcuring, and thus they give so-called "table-top" cures. The accompanying diagram illustrates this point. The importance of this type of cure is seen in the vulcanization of tires, the outside of which although actually heated longer at the vulcanizing temperature, is not overcured, while the inside layers during the same time are properly cured. Furthermore, for this same reason, it is now possible to cure heavy slabs or large sections of rubber, even though rubber is a poor conductor of heat and the outside is heated for a long period. Since rubber has low thermal conductivity and since vulcanization is an exothermic reaction, when a large or thick object is being vulcanized the temperature must be raised slowly and later lowered slowly over an extended period of time.

BLOOM

Sulfur is soluble in both raw and vulcanized rubber. If the amount of uncombined sulfur in a vulcanizate is greater than its solubility the excess crystallizes throughout the mass and on the surface where it forms a gray finely crystalline powder known as "bloom." Bloom does no special harm, but it is unsightly. Therefore, the amount of sulfur and the conditions of cure



PROGRESSIVE CHANGES IN TENSILE STRENGTH OF A NATURAL RUBBER COMPOUND WITH TIME OF CURE

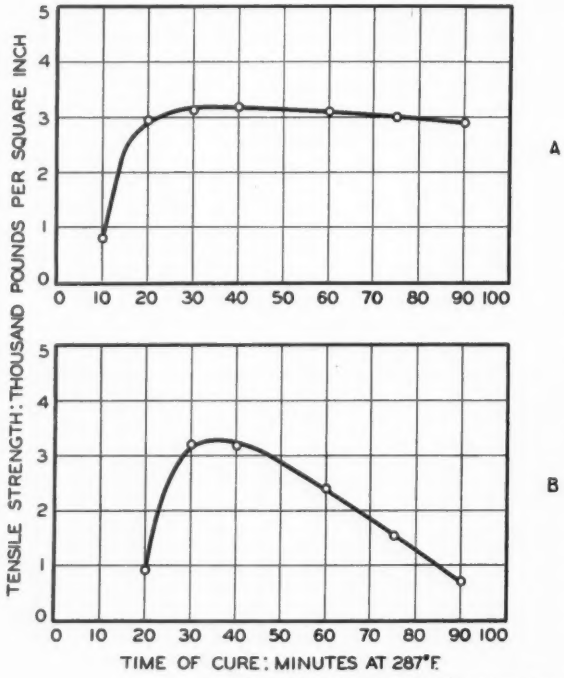
Samples obtained at 15 to 20 minutes are soft vulcanized rubber with an optimum cure. They are highly elastic, and contain about three per cent of chemically combined sulfur. Samples taken at 30 to 60 minutes are still soft, but weak and "short," and generally worthless. As the time progresses, the vulcanizates become less elastic and finally hard and strong. (The recipe is not a commercial one except for hard rubber. For soft rubber only about three per cent of sulfur is used.)*

*SHEPARD, "Symposium on rubber, Regional meeting," *Am. Soc. Testing Materials*, March, 1932, p. 32.

are adjusted in such a manner that most of the sulfur will be "driven home," and thus avoid the formation of bloom. The use of modern accelerators and careful compounding make this possible.

PROTECTION AGAINST AGING

Oxygen and ozone in the air are probably the greatest enemies of rubber, and the use of antioxidants is at present the only known method to combat their action. The conditions under which the rubber is used have much to do with the rate of its deterioration. For



Courtesy of Chemical Publishing Company, Inc.

TENSILE STRENGTH-TIME OF CURE CURVES

A. The desirable type of flat-curing, "table top" tensile strength curve. B. The undesirable type of tensile strength curve.

example, rubber that is kept slightly stretched, at an elongation of 5 to 20 per cent, will for some unknown reason deteriorate much more rapidly than the same rubber at rest or at higher elongations. It is well known that the portion of a rubber tube that is stretched over a nipple rapidly hardens and cracks. Therefore, rubber used in a bent position, like the edge of a stair tread or an automobile running board, is molded in its final shape in order to avoid the rapid deterioration which would otherwise occur under the slight stress in its bent position.

High temperatures also increase the rate of deterioration, and special compounding is employed to produce compositions that will withstand them. Much has been learned in recent years about heat-resisting stocks, because tires and inner tubes on buses and high-speed trucks now run at much higher temperatures than formerly.

Sun cracking or sun checking is still a major problem which has not been solved completely. Sunlight and ultra-violet light produce a hardening of the surface of rubber goods and the hardening is followed by the cracking of the surface. The action is complex and probably consists of some form of polymerization, auto-oxidation and oxidation with ozone, and also overvulcanization from the absorbed heat. Black compounds are affected more rapidly than light-colored compounds. Sulfur bloom on the surface is somewhat beneficial, but the surface bloom of crystals of hydrocarbon waxes used in the original compounding affords the greatest protection.

ANTIOXIDANTS

Antioxidants protect vulcanized rubber against aging, as discussed above, and, furthermore, they increase its resistance to flexing and to the action of heat, and give other properties of value in the mixing of rubber compounds and in the fabrication of rubber goods.

Antioxidants do not act as accelerators and can therefore be included in a rubber compound with them. It happens that some accelerators are also very good antioxidants and can be used for double duty. Antioxidants are used in the same proportion as accelerators, about 1 part to 100 parts of rubber.

The most useful antioxidants are secondary aromatic amines, and condensation products of aliphatic aldehydes or ketones with aromatic amines. Examples are phenyl-β-naphthylamine ("Neozone D" and "Age-rite Powder"), N,N′-di-β-naphthyl-p-phenylenediamine ("Age-rite White"), and a condensation product of acetaldehyde and aniline ("VGB"), and of acetone and diphenylamine ("BLE").

Accelerated aging tests have been devised for predicting the life of rubber goods. They consist of heating strips of the sample in air or oxygen in ovens maintained at definite temperatures for different periods of time. By determining the tensile strengths and comparing these it is possible to predict how well and how long the sample will last.

CHEMICAL PROPERTIES

The rubber hydrocarbon is unsaturated and contains one double bond for each C_5H_8 group. Unsaturation generally means that the substance is very reactive chemically, but this activity is considerably decreased in substances of very high molecular weight. Both raw and vulcanized rubber have very high molecular weights and are surprisingly inactive toward many strong chemical agents.

Concentrated hydrochloric acid acts very slowly but gradually forms a layer of a hard hydrochloride, while the portion inside retains its characteristic rubber properties. Fifty per cent sulfuric acid shows no apparent action, although acid of higher concentration slowly destroys rubber. Tank cars are lined with

rubber for shipment of many corrosive chemicals. Since hard rubber is already chemically saturated with sulfur, it withstands the corrosive action of chemicals to a much greater degree than soft rubber.

CHEMICAL DERIVATIVES

The chemical unsaturation of rubber is taken advantage of in the preparation of several commercially useful products. Oxidation products in which a comparatively small proportion of oxygen is combined with the rubber hydrocarbon are used as adhesives and in paints. Chlorinated rubber, which contains about 66 per cent of chlorine and is both an addition and a substitution product, finds application in corrosion-resisting paints because of its stability toward strong acids and their fumes. Rubber hydrochloride (Pliofilm) can be produced in thin transparent sheets which are useful for packaging and for making raincoats.

RUBBER AND COTTON

There are many cases in which the unique "stretchability" of rubber is not needed, but its resiliency, resistance to abrasion, and impermeability to moisture are needed. In such cases the rubber is supported with cotton fabric. Tires, boots and shoes, tarpaulins, gaskets, diaphragms, hose, and belting are familiar products containing a cotton framework. The cotton imbedded in the rubber, where it is free from the action of air and moisture, has long life and thus can serve its purpose well.

RECLAIMED RUBBER[1]

Worn-out rubber goods are reclaimed by processes which re-soften or re-plasticize them. Vulcanized rubber has never been devulcanized but reclaimed rubber can be vulcanized again, or rather further, and thus used for certain purposes where the first qualities of raw rubber are not required.

The most important process is treatment of the scrap, from which all metal parts have been removed, with a solution of sodium hydroxide at a high temperature and pressure to dissolve the fabric and remove the "free" sulfur, and at the same time with oils to soften the material. It is then washed, dried, strained, and milled into sheets.

Reclaimed rubber contains the original fillers and some of the other ingredients incorporated when the goods were manufactured. That from tires contains about 55 per cent of its weight equivalent to crude rubber. The normal annual production in this country is approximately 200,000 tons. The price varies with the price of crude rubber—from one-quarter to one-third.

PART II—SYNTHETIC RUBBERS

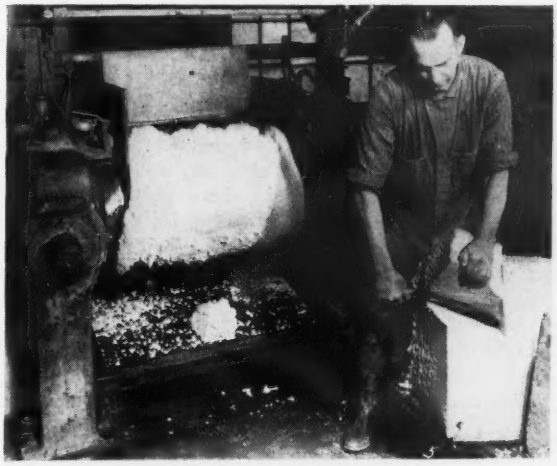
STRUCTURE AND SYNTHESIS

The structure of the rubber hydrocarbon is fairly well understood, although not completely. Its empirical formula is $(C_5H_8)_x$, and its structure is best represented as $(—CH_2\cdot\overset{CH_3}{\overset{|}{C}}:CH\cdot CH_2—)_x$. Since the hydrocarbon isoprene, $CH_2:\overset{CH_3}{\overset{|}{C}}\cdot CH:CH_2$, can be obtained from it by heat decomposition, and since rubber-like products can be prepared by heating isoprene in the presence of a catalyst, rubber is considered to be a polymer of isoprene. These synthetic substances are similar to but not identical with the rubber hydrocarbon, and therefore the statement can be made that rubber itself has never been synthesized. And yet in scientific articles, books, and newspapers, and on the radio the term "synthetic rubber" has been used time and again. The explanation of this apparent anomaly lies in the fact that rubber is now also considered as the name of a *type* of material instead of only a chemical individual. In this sense, rubbers have been synthesized, and the term, "synthetic rubber" is justified.

POLYMERS AND ELASTOMERS

Rubber itself and all the synthetic rubbers are polymers; that is, as indicated by the meaning of the term, they are made up of "many parts." Rubber, as stated above, is probably a polymer of isoprene; that is, it consists of the union of a great many molecules of isoprene. Although the laboratory polymerization of isoprene gives a synthetic rubber, it must not be assumed that the rubber tree makes rubber in the same manner, since isoprene has never been found in the rubber tree, and the mechanism of formation of natural rubber is entirely unknown.

The word elastomers ("elastic parts") is often used for synthetic rubbers.



Courtesy of The B. F. Goodrich Company

WASHING RAW SYNTHETIC RUBBER

The blocks of raw synthetic rubber, each weighing about 110 pounds, are cut up or broken into small pieces and washed and sheeted on a wash mill. Under heat and pressure moisture is wrung out and the lumpy material is squeezed into thin sheets and then cut to standard size and dried.

[1] TRIMBLE, "Reclaimed rubber," J. CHEM. EDUC., 19, 420 (1942).

BUTADIENE POLYMERS

Isoprene is somewhat difficult to make and heretofore has not been a commercial chemical, and synthetic rubbers made solely from it have not been of practical value. However, its chemical parent, 1,3-butadiene $CH_2{:}CH{\cdot}CH{:}CH_2$, is made on a large scale and is the basic material for several synthetic rubbers. Butadiene is a conjugated diolefin, since it is an unsaturated hydrocarbon containing two double bonds in alternate or conjugated positions. When an unsaturated substance polymerizes, part of the unsaturation always disappears. The polymers of butadiene are enormous compounds made up of butadiene residues arranged partly end to end in a closed cycle and having chiefly the structure $(—CH_2{\cdot}CH{:}CH{\cdot}CH_2—)_x$, or they are similar long "open chain" compounds with an extra double bond at one end. These polymers may have molecular weights of at least 100,000, and contain upwards of 1800 butadiene residues. Natural rubber varies in molecular weight from 100,000 to 300,000, and therefore probably contains from approximately 1500 to 4500 isoprene residues.

COMPOSITION OF SYNTHETIC RUBBERS OR ELASTOMERS

The synthetic rubbers or elastomers on the market are quite varied in their chemical composition. A few of them are prepared from two separate starting materials which are polymerized in the same operation to form mixed or copolymers. In these copolymers, the two substances are united chemically in the polymeric chain. Butadiene is generally used as one starting material, and at present the other two materials used commercially are styrene, $C_6H_5{\cdot}CH{:}CH_2$, and acrylonitrile, $CH_2{:}CH{\cdot}CN$. Butadiene and styrene give a synthetic rubber known as Buna S, and butadiene and acrylonitrile give products called Perbunan or Perbunan extra, depending on the proportion of acrylonitrile. Ameripol, Hycar, and Chemigum are also prepared from butadiene copolymerized with substances whose compositions have not been made public. All of these copolymers contain high proportions of butadiene. Butyl rubber is a copolymer in which the butadiene, isoprene in this case, is in the low proportion, only about 2 per cent, and an olefin, isobutene, is in the high proportion.

The copolymers of butadiene and the polymers of chloroprene are usually prepared in the form of an emulsion in water in the presence of a catalyst. The final product is therefore an artificial latex. These latices contain particles which, on the average, are smaller than those in natural rubber latex, and are used in the same general manner for impregnating fabric, etc. The solid elastomer is usually obtained by coagulation with a weak acid, just as natural rubber is obtained.

The chloroprene for neoprene rubber is prepared by forming a dimer of acetylene, namely, vinylacetylene, $HC{\equiv}C{\cdot}CH{:}CH_2$, and adding HCl to this. A rearrangement takes place to give chloroprene, $CH_2{:}CCl{\cdot}CH{:}CH_2$. The chloroprene is also polymerized as an emulsion, and the artificial latex obtained is then coagulated to form neoprene. There are several types of neoprene depending upon the method by which they are prepared and made ready for the market.

The reaction product of ethylene dichloride and alkali polysulfides is also obtained as an artificial latex, which is coagulated to give Thiokol. Thiokol latex has larger particles than those just described. Besides ethylene dichloride, other dichlorides are also used, such, for example, as 2,2′-dichloroethyl ether, $ClCH_2{-}CH_2OCH_2CH_2Cl$, which with sodium tetrasulfide gives Thiokol B; and glycerol dichlorohydrin, $CH_2ClCH{-}(OH)CH_2Cl$, which gives Vulcaplas, an English product.

Koroseal is polyvinyl chloride plasticized with a high proportion of tricresyl phosphate or other plasticizer. Vinyl chloride has the structure $CH_2{:}CHCl$ and can be prepared from ethylene dichloride by the removal of one HCl or from acetylene by the addition of one HCl. Polyvinyl chloride is a white powder with no resemblance to rubber, but when properly plasticized it gives a rubber-like product with many interesting properties.

VULCANIZATION OF SYNTHETIC RUBBERS

As already stated, the commercially available synthetic rubbers vary in their chemical composition, and therefore it is not surprising that their vulcanizing characteristics vary also. The butadiene copolymers are nearest to natural rubber in chemical type and they can be vulcanized with sulfur, zinc oxide, and accelerators more or less as natural rubber is vulcanized. Neoprene is also structurally similar to natural rubber, but it has a chlorine in place of a methyl group, and this makes a difference in its vulcanization. Neoprene can be vulcanized with sulfur, but the sulfur is not really necessary, since vulcanization can be effected by heat alone. It is probable that a trace of oxygen is required and the small amount necessary is no doubt always present dissolved in the material.

Butyl rubber is vulcanized like the other butadiene derivatives, with sulfur, zinc oxide, and an accelerator.

The Thiokols require a metallic oxide like zinc oxide, and sulfur acts as an accelerator!

Polyisobutene or Vistanex is not vulcanizable. It softens with heat and can be molded or mixed with rubber, but it remains a thermoplastic material. Plasticized polyvinyl chloride or Koroseal is also a thermoplastic material and cannot be vulcanized. It retains its shape and properties so long as it is not used above 75°C.

The butadiene rubbers can also be converted into hard rubbers, just as natural rubber, by the use of a large proportion of sulfur. These hard rubbers have higher softening temperatures and less cold flow than those from natural rubber. Neoprene has never been converted into a hard rubber type, and since Vistanex, Thiokol, and Koroseal are not vulcanized with sulfur they are not converted into hard rubbers. Mixtures of Neoprene, Vistanex, or Thiokol with natural rubber and high sulfur give hard rubbers that are flexible.

PROCESSING

Although, in general, regular rubber mills and other machinery can be used with the synthetic elastomers, they cannot be handled the same as natural rubber. They are more resistant to air oxidation, and therefore the oxygen of the air does not cause the same breakdown. Also temperature effects and softening effects with solvents are very different than with natural rubber. Lower temperatures and lower speed ratios of mill rolls, and smaller batches are generally required.

COMPOUNDING

Carbon black and the semi-reinforcing blacks are the most important compounding ingredients for the synthetic rubbers. Without these blacks the compounder would have considerable difficulty. This statement does not mean that good serviceable compounds cannot be made without the blacks, but the compounds with optimum physical properties are made with them. Carbon black gives compounds with high tensile strength, and good abrasion and tear resistance.

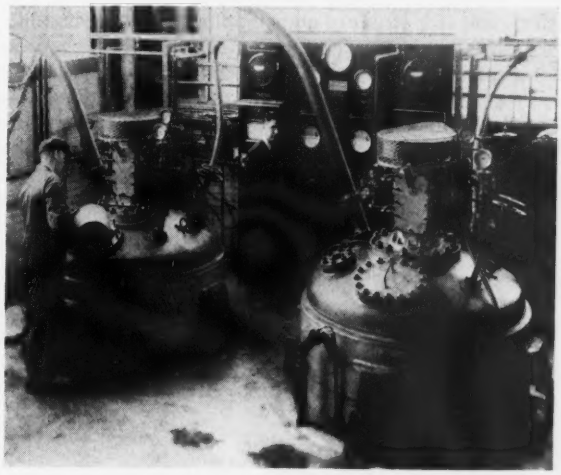
Although the general principles used in compounding natural rubber are applicable to the synthetic rubbers, each synthetic rubber requires special treatments to produce the best results. Besides the milling already discussed, compounding differs somewhat to give proper handling on the calenders and in the extruders, proper "tack" for building-up operations, resistance to heat and abrasion, and other desirable properties.

Softeners are used to a greater extent with synthetic rubbers than with natural rubber, since the synthetic rubbers are tougher than natural rubber.

Since synthetic rubbers show much better resistance to aging than natural rubber, it is not always necessary to use antioxidants for this purpose. However, the synthetic rubbers have a tendency to continue to polymerize in storage, and antioxidants have been found to act as retarders of polymerization. The butadiene copolymers and neoprene generally contain upwards of 2 per cent of an antioxidant, phenyl-β-naphthylamine. In heat-resistant compounds it is necessary to add more of the antioxidant incorporated originally in the stock, or to add another antioxidant to further retard the polymerization and prevent hardening.

PROPERTIES AND APPLICATIONS OF SYNTHETIC RUBBERS

In tensile strength, stretchability and speed of comeback, resilience, and lowness of permanent set, natural rubber is still king of the rubbers, but for good aging and for resistance to abrasion, to sunlight, to the action of oils, fats, and solvents, to the coronal discharge, and to the diffusion of gases, the synthetic rubbers have already wrested the crown from natural rubber, and in these fields at present stand supreme. Improvements in synthetic rubbers are being made rapidly, and just as the tensile strength and resistance to abrasion have become superior in some synthetic rubber compounds, so other properties may soon be "taken over" and surpass those of natural rubber compounds. Synthetic rubbers are too new to hazard predictions about them. However it must be remembered that natural rubber is cheap and available under normal conditions, that much more is known about using it than the synthetic rubbers, and that continued work is constantly improving its compounds. A synthetic rubber cannot be substituted directly for natural rubber in a specifically designed compound, but its own characteristics should be considered and used to their full advantage for the desired application.



Courtesy of The B. F. Goodrich Company

POLYMERIZATION AUTOCLAVES

Polymerization is the chemical term describing the process which combines many small molecules to form complex molecular units, like the joining of links to form a chain. The butadiene and other ingredients which go into the production of synthetic rubber are polymerized in large steel vessels in which they are agitated and emulsified in a soap solution under pressure. The process results in the creation of a material with a molecular structure similar to that of natural rubber.

Buna S is used for tire treads, since it shows extraordinary resistance to abrasion. Chemigum and Ameripol or Hycar OR also show very good resistance to abrasion and are also used for tire treads.

Natural rubber is more resilient than synthetic rubbers, and tires made of natural rubber show a lower build-up of heat under rapid deformation. Technically speaking, natural rubber compounds show the lowest energy loss due to hysteresis. As tires bound over the road the rubber becomes hot. However, although synthetic rubbers become hotter they withstand the action of heat better and therefore synthetic rubbers are being used advantageously and extensively on buses and trucks.

Thiokol A is not so good for abrasion resistance, but it is the outstanding synthetic rubber for resistance to swelling in oils and fats. Hycar OR (the OR stands for "oil resistant"), certain varieties of Chemigum, Neoprene, Butyl and Koroseal resist swelling in different types of solvent. Also they show excellent re-

sistance to the action of the coronal discharge, to the diffusion of gases, to the action of corrosive chemicals, and to flex-cracking. Because of these properties they have found use in places where natural rubber compounds were unsatisfactory or often could not be used at all.

A few examples of their use where natural rubber cannot be used are: as linings for airplane gasoline tanks, for equipment in deep oil well drilling, in printing rolls for the new quick-drying inks, for conveyor belts for oil-treated coal, in power cables in mines and on ships and airplanes where it is essential that materials be used that are unaffected by oils and do not propagate fire, and for tubing and diaphragms for handling chlorine gas, ozone, and sulfur chloride. The success of airplane deicers depends upon the Neoprene veneer which protects the underlying rubber from deterioration in sunlight. Many other examples could be given but these are enough to show how the new synthetic rubbers are finding places all their own, and under normal conditions are able to compete with natural rubber entirely on a quality basis.

ACKNOWLEDGMENT

The author is grateful to Mr. C. L. Warwick, Secretary-Treasurer, American Society for Testing Materials, Philadelphia, Pennsylvania, for his kind permission to reprint portions of the author's Edgar Marburg Lecture on "Natural and synthetic rubbers," which was presented at the Forty-fourth Annual Meeting of the Society, 1941.

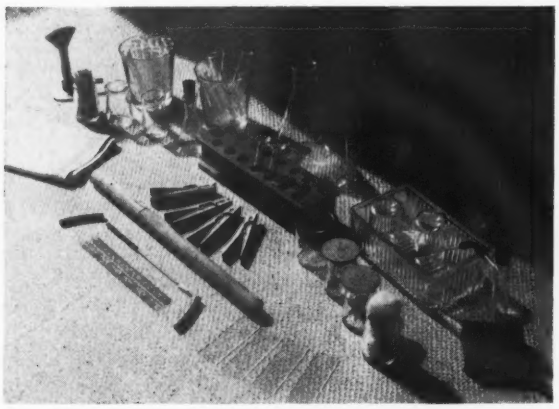
BIBLIOGRAPHY

(1) DAVIS AND BLAKE, Editors, "The chemistry and technology of rubber," Monograph No. 74, American Chemical Society, Reinhold Publishing Corp., New York, **1937.**
(2) FISHER, "Rubber and its use," Chemical Publishing Co., Inc., Brooklyn, N. Y., **1941.**
(3) HAYNES AND HAUSER, "Rationed rubber and what to do about it," Alfred A. Knopf, New York, **1942.**
(4) MEMMLER, Editor, "The science of rubber," Translation edited by R. F. Dunbrook and V. N. Morris, Reinhold Publishing Corp., New York, **1934.**
(5) NAUNTON, "Synthetic rubber," Macmillan Co., New York, **1937.**
(6) BALL, Editor, "The Vanderbilt rubber handbook," 8th ed., R. T. Vanderbilt Co., 230 Park Ave., New York, **1942.** (This practical handbook contains much valuable information not only on natural rubber but also on synthetic rubbers.)

SEMIMICRO EQUIPMENT FOR THE ELEMENTARY LABORATORY

SHIRLEY GADDIS *Eureka College, Eureka, Illinois*

THE ACCOMPANYING illustration shows the apparatus needed to stock the desk for a course in



general chemistry taught on a semimicro scale. The unusual pieces of equipment are:

1. Small cream jars, used by cafeterias for honey, marmalade, etc. Since they will stand heating, they can be used for extra beakers or flasks, or for gas-collecting bottles.
2. An uncovered 50-ml. beaker, in place of the usual evaporating dish or crucible, for quantitative work.
3. Clothespins for test-tube holders. Data can be recorded on the sides on the pins and then erased.
4. Toothpicks, used as splints for testing gases.
5. Whiskey glasses (5 cents each) are convenient holders for the 36 test tubes.
6. A glass butter dish for a pneumatic trough. Milk bottle caps, instead of glass plates.
7. The apparatus for the generation and collection of gases is shown at the right. It can be used to prepare H_2, CO_2, C_2H_2, SO_2, Cl_2, HCl, and Br_2. A side-arm test tube with delivery tube attached proves to be more satisfactory than the usual thistle-tube arrangement.
8. Two Barber tubes and cotton are supplied.

The inventory cost of the apparatus in the elementary desk is cut to $3.87. Non-returnables are 35 cents. The apparatus fits in a drawer 12 by 10 by 4 inches, which is brought by the student to a desk permanently equipped with burner tubing, file, ring stand, ring, wire gauze, hand balance and weights, and a small bottle of glycerin to lubricate rubber stoppers and tubes.

A boat deck cleat has been designed of glue-laminated wood, replacing iron which is needed for war production. The laminated cleat is stronger by weight and less expensive than the iron cleat.

A Simplified Electronic Thermoregulator

WARREN E. GILSON and HAROLD A. WOOSTER

University of Wisconsin Medical School, Madison, Wisconsin

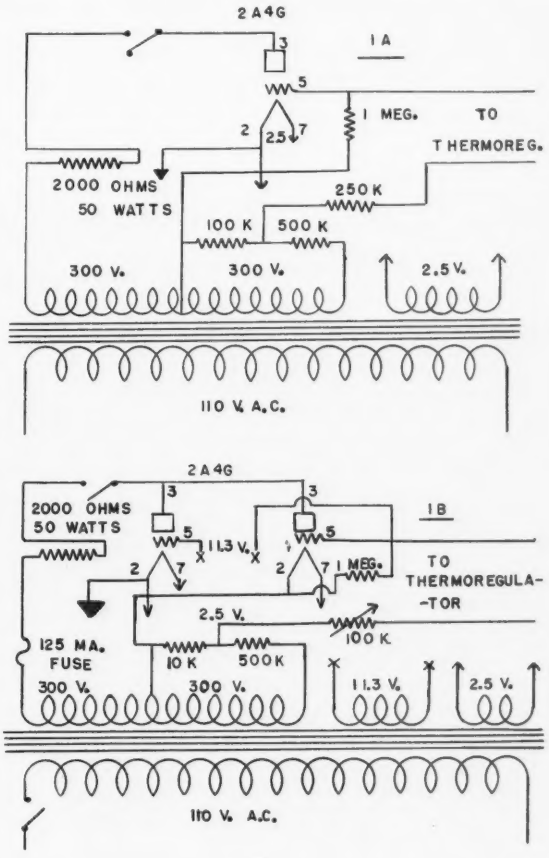
IN RECENT years several articles on thermoregulators have been published, describing the use of vacuum tubes for the control of relays, and thus indirectly, of heating elements (*1–6*). When relays are used in this manner, it is necessary to renew the contact points quite frequently, especially if the electronic circuit does not have a time delay feature to prevent chattering caused by slight vibration producing intermittent closing of the mercury contacts. This difficulty is obviated by the use of a thyratron, eliminating the relay entirely, as well as providing a quieter, more reliable, and generally more elegant control.

The advent of small thyratrons (the 2A4G) and their wide use in pinball machines and other amusement devices has brought their price to a reasonable level. Large thyratrons have been used in commercial practice for many years for the convenient and efficient control of power. Inasmuch as a small water bath requires only 10 to 15 watts of electrical energy for thermostasis at the conventional temperatures, it seemed desirable to construct a thyratron control, regulated by a mercury-toluene thermoregulator. The grid current of a thyratron is a fraction of one milliampere, much less than that required for satisfactory operation of a relay. The prime advantage of this is the greatly lessened current at the mercury contact, and the consequently retarded formation of oxide at this point. We have used such a thyratron control for over three months, with entirely satisfactory service. The accuracy of contro is dependent on the thermal characteristics of the system used. In our case the regulation was within plus or minus 0.05°C.

A thyratron is a gas-filled tube, usually a triode, which is non-conducting when the grid is sufficiently negative. As the grid becomes less negative the tube "breaks down," or "fires," ionization occurs, and plate-filament current flows. This is indicated by a blue glow between the plate and the cathode. The grid then loses control of the plate current, which can be stopped only by momentarily removing the plate voltage. The voltage drop in a thyratron is approximately 15 volts, and is almost independent of the plate current. For further information on the 2A4G consult the "Sylvania Tube Manual."

Figure 1A shows the simplest form of our circuit, as first constructed. It is relatively inexpensive, the parts costing about $6. The circuits which have been described for such control of laboratory water baths generally use either batteries to bias the thyratron (*7*), or use the thyratron to control a relay. Because of the small amount of energy needed in this application, no relay is necessary. The use of batteries where A.C. is available is ordinarily undesirable. For these reasons it seemed logical to apply phase control (as used in a much more complicated form in welding circuits), thus making it possible to use a small power transformer of the replacement type for control voltage as well as heating current.

The circuit operates as follows: if the mercury contacts are open, the grid is at cathode potential and plate current will flow during the half of the cycle in which the plate is positive with respect to the cathode. When the plate current passing through the heating coil has warmed the bath to the required temperature, the mercury column will rise to close the contacts. This brings



the grid to a negative potential during the part of the cycle when the plate is positive, and thus prevents conduction. This occurs because the opposite ends of the

high-voltage winding are 180 degrees out of phase with respect to the center tap.

Figure 1B illustrates a more complex circuit in which the operation is safeguarded against tube failure. One of the tubes will operate in preference to the other until it fails. The other tube will then assume its function, thus indicating the necessity of replacing the first tube. This should be quite infrequent, as the tubes are guaranteed for 90 days of continuous use.

In some cases R1 must be adjusted on an empirical basis when the circuit is first placed in operation. This may be done by trial of various fixed resistors, as in 1A, or by the use of a variable resistor, as in 1B. For protection of the contacts it is desirable to use the highest resistance which will give satisfactory operation. The switch in the plate circuit is for the purpose of protecting the cathode of the tube. This switch should not be closed until several seconds after the filament voltage is applied. The heating element is a conventional 2000-ohm, 50-watt bleeder. It is supported in a brass cylinder by glass spacers at each end. This cylinder is tightly stoppered and partially immersed in the water bath.

The voltage applied to the mercury contacts is not dangerous because it is only a small part of the secondary voltage, and is further rendered innocuous by the high resistance in series with it.

The transformer should be able to furnish at least 60 milliamperes, but should not have a voltage higher than 300 volts on each side of the center-tap. If larger amounts of power are necessary, a larger thyratron may be used, or a relay may be put in the plate circuit in place of the heating element.

Understanding of the circuit is not necessary for successful construction and operation, as it is merely necessary to wire the numbered connections on the octal socket to the points indicated. If difficulty arises, a radio service man acquainted with pinball machines or a physicist working with Geiger counters should be able to find the trouble readily.

When they are again available the 2050 should be used in preference to the 2A4G, because of lesser grid current and greater sturdiness.

LITERATURE CITED

(1) HAWES, *Ind. Eng. Chem., Anal. Ed.*, **11**, 222–3 (1939).
(2) RUDY AND FUGASSI, *ibid.*, **12**, 757 (1940).
(3) SERFASS, *ibid.*, **13**, 262–3 (1941).
(4) *Ibid.*, **13**, 352–3 (1941).
(5) WADDLE AND SAEMAN, *ibid.*, **12**, 225 (1940).
(6) REDFERN, *ibid.*, **14**, 64 (1942).
(7) DANIELS, MATHEWS, AND WILLIAMS, "Experimental physical chemistry," 3rd ed., McGraw Hill Book Company, Inc., New York, **1941**, p. 416.

REVISION OF THE INDICATOR METHOD OF CLASSIFYING ACIDS AND BASES IN QUALITATIVE ORGANIC ANALYSIS

DAVID DAVIDSON *Brooklyn College, Brooklyn, New York*

THE INDICATOR reagents recently recommended for use in qualitative organic analysis[1] possess satisfactory stability over a period of a year except in the case of the B-II reagent. The difficulty in this case is due to the ease with which the less acidic sulfonphthaleins such as thymol blue undergo conversion to dimethyl ethers by means of methanol.[2]

It is now recommended, therefore, that the B-II indicator reagent be prepared without thymol blue, 25 ml. of methanol being substituted for the 25 ml. of thymol blue stock solution previously prescribed. The resulting change in the color chart of Table 5, page 225, involves the extension of the yellow zone of the weak bases to the right-hand edge of the chart since the red zone no longer appears.

The thymol blue stock solution (0.1 per cent in methanol) which is employed in preparing the A-II indicator reagent should be made up with sufficient 2 *M* potassium hydroxide (in methanol) to convert most of the indicator to its basic form (blue). 0.3 ml. per 100 ml. of stock solution is adequate.

This opportunity will be taken to point out several typographical errors which occurred in the original article as well as in a companion article.[3]

Page 160, Example 2, last line. Read "weak" for "intermediate."

Page 160, Example 3, next to last line. Insert "ion" after "dipolar."

Page 222, Table 1. Read "10^{-14}" for 10^{-1}."

Page 224, Figure 2, horizontal axis. Read "14" for "4."

Page 224, second column, line 17. Read "5.4" for "8.6."

Page 226, first column, next to last paragraph. Read "sulfonimides" for "sulfonamides."

[1] DAVIDSON, *J. Chem. Education*, **19**, 221 (1942).
[2] ORNDORFF AND CORNWELL, *J. Am. Chem. Soc.*, **48**, 981 (1926): ORNDORFF AND SHAPIRO, *ibid.*, **46**, 2856 (1924).
[3] DAVIDSON, *J. Chem. Education*, **19**, 154 (1942).

A Simplified Electrosmosis Apparatus

JERMAIN D. PORTER

Lebanon Valley College, Annville, Pennsylvania

FUNDAMENTALS

IF A NARROW tube is filled with liquid and a difference of electrical potential applied to its ends by means of electrodes connected with a battery, liquid may under favorable conditions be observed to flow through the tube. This is the phenomenon of electrosmosis. If, instead, the solid material of the tube is dispersed as fine particles in the liquid, a potential difference applied between electrodes in the liquid causes the particles to move in a direction opposite to that of the liquid in electrosmosis. This phenomenon, in which solid surfaces move through a liquid under the influence of an applied potential, is electrophoresis, and it is evidently the inverse of electrosmosis, in which it is the liquid which moves past the solid surface.

Aside from the external potential difference applied by means of electrodes immersed in the liquid, a fundamental requirement for both phenomena is an intrinsic potential difference between the liquid phase and either the solid surface itself or an adsorbed layer rigidly held upon it. This potential difference arises from a separation of charges at the phase boundary, resulting in the formation of a so-called electrical double layer. The origin, composition, and structure of the double layer, and the magnitude of the effective potential difference across it, called the zeta (ζ) potential, depend upon the nature of the two phases in contact. Frequently in water and aqueous solutions the double layer is formed by the preferential adsorption of ions of one sign or the other upon the solid. If the negative ions present are more strongly adsorbed than the positive, the surface acquires a net negative charge, and the neighboring liquid is left with a positive charge. Figure 1 shows in idealized form why electrosmosis and electrophoresis occur, and the relation between them.

A porous diaphragm is often used in electrosmotic studies instead of a single narrow tube. It is equivalent to a large number of capillary tubes in parallel.

The quantitative theory of electrosmosis is discussed in the textbooks (*1* through *4*), and leads to the equation

$$V = \frac{A\zeta ED}{4\pi\eta L} \qquad (1)$$

A = Cross-sectional area of tube, or total cross-sectional area of pores extending through a diaphragm
D = Dielectric constant of the liquid
E = Applied potential difference
ζ = Zeta potential of the double layer
η = Viscosity of the liquid
L = Length of tube or thickness of diaphragm
V = Volume of liquid electrosmotically transported in unit time

EXPERIMENTAL

Electrosmosis is always discussed in colloid chemistry courses, but rarely demonstrated. When we assigned a group of students the task of setting up a workable electrosmosis apparatus, we found that the types described in the laboratory manuals were unsuitable.

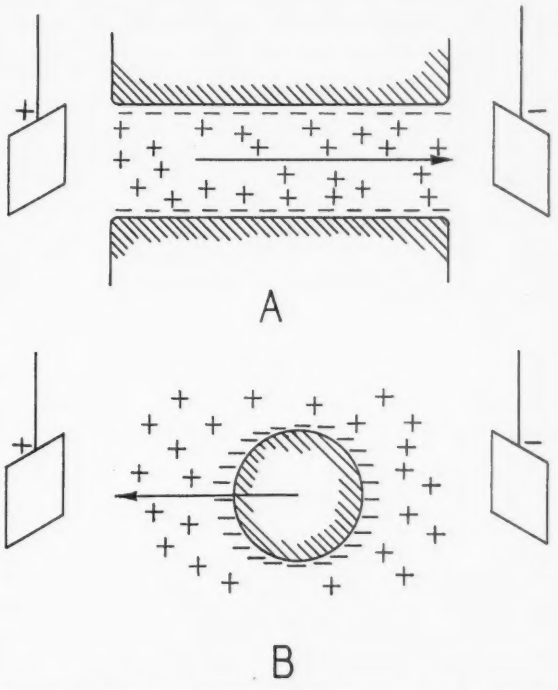


FIGURE 1.—RELATION BETWEEN ELECTROSMOSIS AND ELECTROPHORESIS

A. Electrosmosis of a liquid through a tube the wall of which has adsorbed negative ions preferentially. The liquid, left with a net positive charge, moves toward the cathode.

B. Electrophoresis of a solid particle through a liquid. As in A, the solid has preferentially adsorbed negative ions, but in this case it is free to move.

Some required special apparatus which was not easily constructed, some called for inconveniently high voltages, and one attractively simple arrangement was defective in design in that the diaphragm cross section was too small, and that evolution of gas at the electrodes obscured whatever motion of liquid there may have been.

We set about, therefore, designing an electrosmotic cell which could be easily assembled from commonly available materials. We wished to show, using not

more than two or three 45-volt B-batteries, the dependence of the electrosmotic flow upon polarity and voltage, upon the nature and concentration of the solution, and upon the material of the solid phase. We did not insist upon obtaining numerical values of the ζ potential.

The use of a porous diaphragm rather than a capillary tube makes possible the study of a greater variety of solids. Equation (1) shows that a large total pore cross section favors a rapid transport of liquid. If, however, we make the individual pores large, the rate of hydrostatic backflow through their central portions will be too great. Hence we need small pores, but a sufficient number of them to give a large total cross section. The occurrence of L in the denominator suggests making the diaphragm thin. We adopted the main features of Gyemant's apparatus (*5*). The electrosmotic flow occurs between a crystallizing dish and a bell dialyzer through a diaphragm covering the mouth of the dialyzer. A wide-mouthed bottle cut off just below the shoulder is a suitable substitute for the dialyzer.

The active diaphragm is a thin layer of powder of the material to be studied, *e. g.*, kaolin, infusorial earth, alumina, ferric oxide, or bone black. The powder is spread in an even layer 2–4 mm. thick on a sheet of filter paper so as to cover an area the size of the mouth of the dialyzer. The diameter of the paper should exceed that of the dialyzer by about 4 cm. The layer of powder is covered with a second sheet of filter paper, and the resulting sandwich is enclosed between discs of loosely woven cloth to prevent it from tearing when wet. The dialyzer is then placed on top of the pile, and the edges of the cloth and filter paper are folded up around its rim and held tightly by several stout rubber bands. The cloth discs should be drawn taut.

The filter paper and cloth alone would serve as an electrosmotic membrane, but their high porosity permits such rapid backflow that a control experiment omitting the powder shows only a small net transport of liquid. The slight error due to this cause could be decreased by using a thicker powder layer, at the expense, however, of a reduction in the rate of flow.

Figure 2 shows the accessories needed for producing and detecting the electrosmotic flow. The dialyzer K and the vial A_2 are supported by clamps. Current is led into the dialyzer through the salt bridges C_2 and C_3, containing approximately 6 per cent agar in 2 M potassium chloride. If a metal electrode were inserted directly through the stopper, gas bubble formation might obscure the electrosmotic flow, and heavy metal ions might contaminate the solution. Potassium chloride tends to diffuse out of the gel at the end of the bridge. This is undesirable because the electrolyte reaching the diaphragm generally lowers its ζ potential, and because the decreased concentration in the end of the bridge raises its resistance and hence lowers the

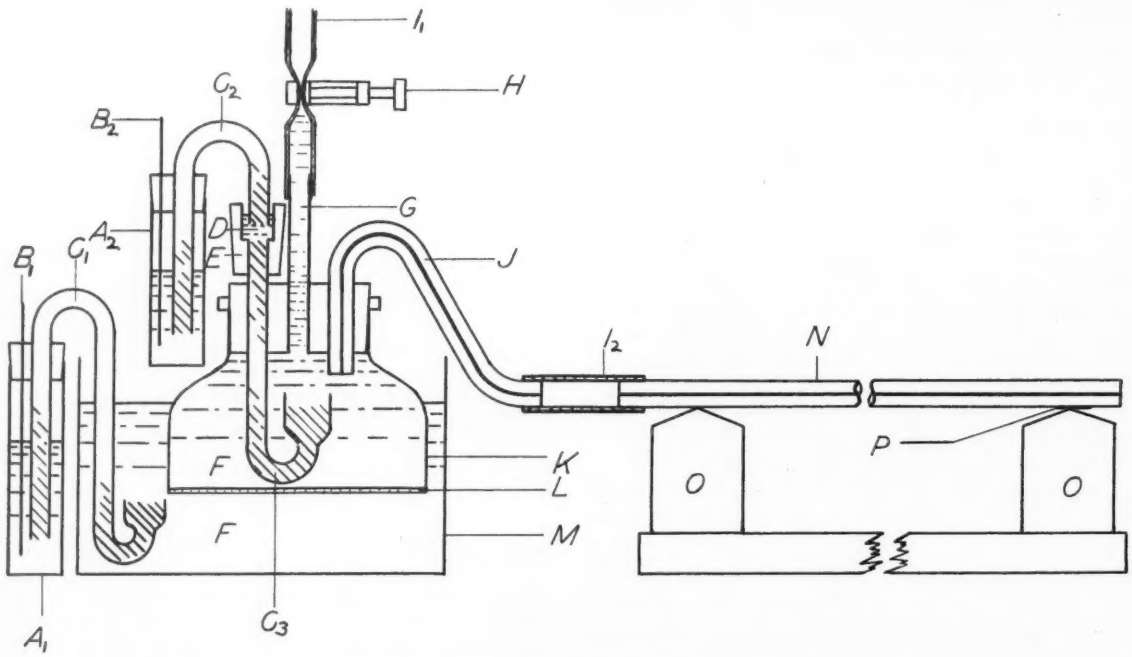


FIGURE 2.—DIAGRAM OF ELECTROSMOSIS APPARATUS

A_1, A_2 = vials containing $CuSO_4$ solution. B_1, B_2 = copper wire electrodes. C_1, C_2, C_3 = agar-KCl salt bridges. D = KCl solution. E = cork hollowed out to contain D. F = water or solution being subjected to electrosmosis. G = glass tube used when filling apparatus. H = screw clamp. I_1, I_2 = rubber tubes. J = capillary tubing. K = bell dialyzer or wide-mouth bottle cut off below shoulder. L = powder diaphragm supported between filter paper sheets reinforced with cloth. M = crystallizing dish. N = capillary tube in which motion of meniscus is observed. O = wooden support. P = copper foil shim to adjust slope of N.

potential drop across the diaphragm. To reduce loss of electrolyte, the inner end of C_3 is enlarged, and the gel is scooped out to a depth of several millimeters, forming a hollow in which the diffusing salt is held. C_2 and C_3 are connected by a few drops of potassium chloride solution contained in a hollowed-out cork E. If a rubber connector is used instead, it is difficult to avoid trapping an air bubble inside it.

Flow of liquid into or out of the dialyzer through the diaphragm is indicated by changes of liquid level in the capillary tube N. To magnify the motion of liquid in it, N is only very slightly inclined by means of a copper foil shim P under its outer end. A rise of about 1 in 250 is sufficient. The tube is held to the supports O by a rubber band running over the top of each pillar between brads driven into its front and back faces. A narrow strip of millimeter cross-section paper fastened to a rod is laid along it to serve as a scale.

To fill the apparatus with liquid, I_2 is closed with a clamp, and I_1 is opened. M is filled with the liquid to be studied, and gentle suction is applied at I_1. When the liquid has filled K and risen into G, H is closed. Then suction is applied at the far end of N and the clamp on I_2 is removed, permitting the capillary tubes to fill with liquid. No air bubbles separating slugs of liquid should remain in the capillary tubes. The meniscus in N is brought to a standstill at a convenient place by varying the height at which K is clamped, by changing the liquid level in M, or by slipping thin sheets of cardboard under the base of the support. With no applied potential, the motion of the meniscus should be less than 1 mm. per minute. It is very important that N be clean so that the meniscus moves easily through it. It may conveniently be kept in chromic acid cleaning solution when not in use.

Two or three B-batteries in series to give 90–135 volts are connected through a reversing switch to the electrodes B_1 and B_2. A milliammeter, though not essential, is a great convenience to indicate whether or not the circuit is properly closed.

To make roughly quantitative comparisons, we start a stop-watch at the moment of closing the switch and at the same time read the position of the meniscus on the scale. At the end of each of four two-minute periods we reverse the polarity and simultaneously read the scale. Figure 3 shows a readily interpreted method of plotting the results. The vertical amplitude of the oscillations indicates the magnitude of the ζ potential, and from the direction of flow for a given polarity, the sign of the charge on the diaphragm may be deduced. A line sloping upward represents an increasing scale reading, that is, liquid flowing into the dialyzer. If this occurs when the inside electrode B_2 is negative, the liquid must be positively charged with respect to the material of the diaphragm, which is therefore negative with respect to the particular liquid being studied.

The data plotted in Figure 3 were obtained with a diaphragm of infusorial earth in contact first with distilled water, and then with thorium nitrate solutions of several concentrations. The applied potential was 135 volts. The graphs show that in distilled water the infusorial earth was negatively charged. In 10^{-6} and 10^{-5} M thorium nitrate solutions the negative charge was considerably reduced, and in 10^{-4} M solution it was entirely neutralized by the strongly adsorbed positive thorium ions. A further increase in concen-

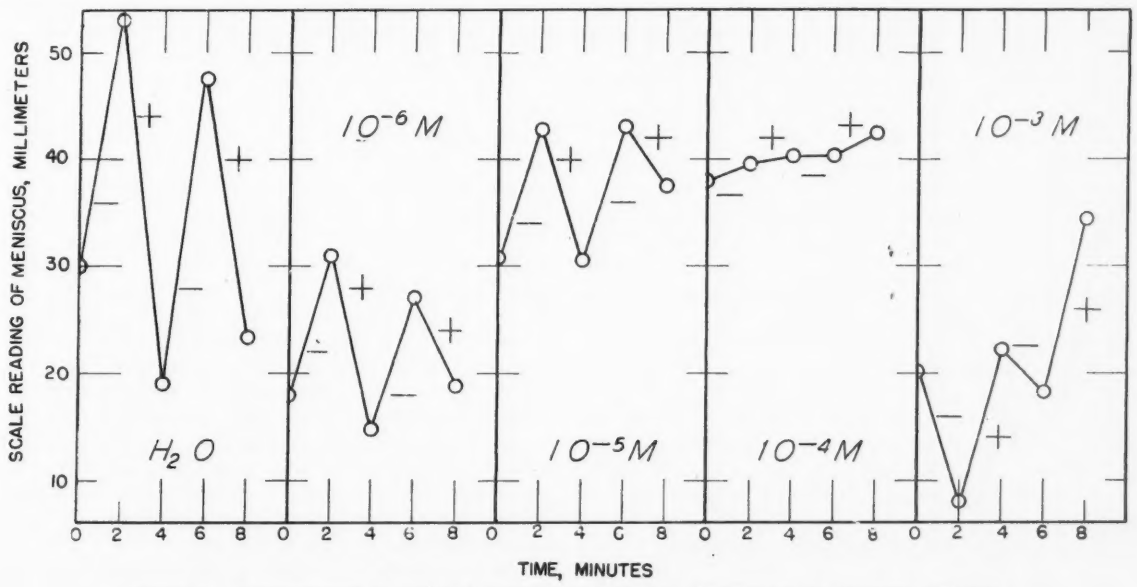


FIGURE 3.—ELECTROSMOSIS OF $Th(NO_3)_4$ SOLUTIONS THROUGH A DIAPHRAGM OF INFUSORIAL EARTH

Position of meniscus is plotted against time, and the polarity is reversed every 2 min. An increase in the scale reading of the meniscus indicates liquid flowing into the dialyzer. The signs given refer to the inner electrode (B_2 of Figure 2). An inward flow of liquid when B_2 is negative shows that the liquid is positive and the diaphragm therefore negative.

tration to 10^{-3} M increased the adsorption of thorium ions and made the infusorial earth positive with respect to the solution. The upward trend of the curves for the two most concentrated solutions seems to be due to the heating effect of the comparatively large currents (15–30 milliamps.) which flowed through them.

All the data plotted in Figure 3 were obtained without renewing or removing the diaphragm. In making such a series of runs it is essential to work from the lower to the higher concentrations, since desorption may not occur readily. It is advisable to draw a little of each new solution through the membrane and expel it again before filling the dialyzer. This serves to eliminate at least a portion of the potassium chloride escaping from the salt bridges. While changing from one solution to another, I_2 may be clamped shut to retain the liquid in the capillary tubes. When a different solute is to be used, a new diaphragm must be prepared.

Other experiments will be suggested by the literature on electrokinetics.

ACKNOWLEDGMENT

The work upon which this paper is based was begun at Union College, Schenectady, New York, and thanks are due to Professor Charles B. Hurd for the use of laboratory facilities, and to Messrs. Armand Cammarota, Robert Davison, and Solomon Penner for assistance in its early stages.

LITERATURE CITED

(1) BANCROFT, "Applied colloid chemistry," 3rd ed., McGraw-Hill Book Co., New York, **1932**, pp. 274–5.
(2) KRUYT, "Colloids," translated by van Klooster, 2nd ed., John Wiley and Sons, Inc., New York, **1930**, pp. 82–3.
(3) FREUNDLICH, "Kapillarchemie," 2nd ed., Akademische Verlagsgesellschaft m. b. H., Leipzig, **1922**, pp. 326–30.
(4) WEISER, "Colloid chemistry," John Wiley and Sons, Inc., New York, **1939**, pp. 205–6.
(5) GYEMANT, "Electroendosmose und Ionenadsorption," *Kolloid-Z.*, **28**, 103–14 (1921).

Opportunities for Women in Chemistry[1]

LOIS W. WOODFORD[2] *American Cyanamid Company, Stamford, Connecticut*

NO LONGER ago than September, 1939, at the Boston meeting, the Division of Chemical Education sponsored a Symposium on Training and Opportunities for Women in Chemistry. These papers[3] are an excellent background for the present discussion, and the student seeking wider information regarding the general situation, and specific fields of work as they existed in normal times, is advised to read them carefully. In short, the girl intent on using her training in chemistry to earn her livelihood had apparently found it necessary to turn to borderline occupations. High-school teaching (16.1 per cent), medical technician (14.6 per cent), study (17.4 per cent), marriage (13.6 per cent), and non-chemical or unknown interests accounted for about eighty per cent of the women chemistry majors of the preceding five years. Less than five per cent were listed as engaged in "industrial research" or as "industrial technician" (4.7 per cent), and about the same number (4.8 per cent) in library work and positions as chemical secretary. Facing facts as they stood at that time, the most cheerful optimist had to admit that the woman chemist's place in the industrial chemical world was none too secure. The industrial chemical laboratories, large or small, were closed to all but the most persistent or the most fortunate.

Our entry into the war changed employment conditions with startling suddenness. The demands of the war production program have taken experienced men from their usual desks to organization work in Washington or elsewhere, and the younger chemists and chemical engineers, the laboratory workers, into production and control jobs in our great munitions plants, or to carry on confidential research projects under the auspices of the National Defense Research Committee. The Selective Service laws contain an occupational deferment plan for essential workers, and specific regulations issued by the Director[4] place chemists, chemical engineers, physicists, and certain other groups of scientists among the critical occupations in which an acute shortage of manpower exists. Up to the present time comparatively few well-trained chemists have actually been drafted into military service; a somewhat larger number have gone in by way of the Officer's Reserve Corps; some have found it necessary to change positions to bring their work closer to the war effort; many eligible for deferment have found irresistible the patriotic impulse to enlist in some front-line activity.

Alert executives foresaw this situation during the period of defense preparations and hastened to build up their chemical research and operating staffs. By the first of the year 1942 it was apparent that the new crop coming out of the colleges and universities in June would fall far short of the demand.

War conditions had created a *golden* opportunity for women chemists. Secretary Parsons and the Employment Clearing House issued an urgent call for women

[1] Presented before the Division of Chemical Education, at the 104th meeting of the A. C. S., Buffalo, New York, September 9, 1942.
[2] Stamford Research Laboratories.
[3] JOURNAL OF CHEMICAL EDUCATION, December, 1939.
[4] *Chem. and Eng. News*, **20**, 837 (July 10, 1942).

chemists to meet the emergency, but the number responding has been discouragingly small. This unprecedented demand precipitated an unheard-of situation in the women's colleges and coeducational institutions. Many large industrial organizations sent their scouts especially to interview the women majoring in chemistry, and those who had the seal of approval of the department head were able to choose between several good offers before the day of graduation arrived. Reports coming in from various sources indicate that at present a well-equipped unemployed woman chemist is as hard to find as the proverbial needle in the hay-stack.

Is there an untapped source of supply of women graduates of earlier years who have kept up with their science, the ever-changing new developments, and the all-important technic that is quickly lost through lack of practice? It is very doubtful. An estimate of the total number of women trained in chemistry (based on the number of feminine Christian names appearing in the current A. C. S. Directory, for want of a better guide) indicates the ratio of women to men is about one to twenty. Reducing our deductions to the limit of absurdity, this means that in the dire need of the moment each woman may have to replace nineteen men in chemical work. We can turn about and say with some justification, "Well, you men have brought this situation upon yourselves. For years you have discouraged in every way possible any girl who expressed an interest in following a chemical career."

Let us change the emphasis on the words of our subject, and interpret the theme as a challenge to women chemists to prove that they are ready, and that they can meet the obligation thrust upon them by war's circumstances. That is a serious challenge! Employers are accepting the entrance of women into industrial laboratory work with grave misgivings. To find a chemical position at the present moment is the simplest thing in the world; to hold on to it while we are in the midst of war preparations is going to require only a minimum of effort on your part; to carve out a place for yourself so secure that you can hold it when the days of keen competition return is quite another matter. Perhaps you think it should be easy, because you have received the same training as did the boys you are replacing, and in the meantime you will have had one or two, or as many years as are required to settle this world affair, to consolidate your position and grow in value to your employer. But you will have an up-hill time of it. Your employer regards you as something he has picked up on the bargain table; and your men associates regard you as an intruder in their domain. This is not all your fault, but it must have been built up by your predecessors somewhere along the line, for a very definite prejudice does exist against women, especially in industrial chemical research. Somehow they are considered perfectly capable of carrying out routine functions, particularly if they are working in a more or less isolated group of their own. Presumably your training is all that could be desired: the fundamental courses in chemistry, biology, physics, mathematics, German, and such other accessory and supporting courses as go to make a well-trained major in our stronger chemistry departments. You have been able to obtain good references from the head of the department and a transcript showing a preponderance of A's and B's in your course work. Nevertheless, you should be told that success or failure depends more on your personal characteristics than on any other one factor. You must remember that your conduct each day, your attitude toward your work, and more particularly toward your associates, will decide your future place in an industrial organization. You have entered the man's business world and you will have to play the game by the long-standing rules. Some of the little things that can happen to upset your whole career seem rather small in themselves. The chemical laboratory is not the place to display a case of temperament, or selfishness, or nerves. The man who is responsible for your work-day expects your thoughts to be on your work a reasonable amount of the time, and that reasonable amount does not make much allowance for habitually making social visits among your friends in other parts of the building, for planning your evening meal, or jotting down the details of your wedding plans if you have not yet reached the altar, or even telephoning one of the other girls and two of the boys in order to make up a bridge table for the evening. Even more serious than time squandering (on which women do not have a monopoly) is the habit of wearing your feelings on your sleeve and getting terribly upset and hurt over a critical comment, undoubtedly meant as a helpful suggestion. Perhaps you have come from a position in a smaller group, where there has been greater independence of action. Can you adapt yourself to new conditions and not get in other people's hair by wanting everything done in the way to which *you* were accustomed? All of us women are told that we fail to see our work, and particularly any criticism of it, from an objective point of view. We must train ourselves to do this if we are to work side by side with the men. If you will control these feminine impulses, and bring into use some other feminine attributes, you can make the way easy for yourself and for those about you. If you but knew it, that boss of yours is a bit wary himself as to just how to handle you. The good man's inherent chivalrous instincts are probably in conflict with his understandable desire to give you a good he-man cussing out and let that end the matter. A quiet dignity, an even disposition, and an outward calm under the most trying circumstances will bring results far greater than can be obtained with an outburst of temper, a hasty retreat to hide unruly tears, or a sullen moodiness which lasts for days and throws the whole group into confusion.

So much for personality within a laboratory, but first impression is often lasting and always hard to change. Was your written application a true revelation of your habits? Was it neat and accurate in detail; were there misspelled words? It probably got by under present conditions of supply and demand. Those who conduct personal interviews are unanimous in their

amazement at the careless approach and evident inattention to details of dress and manners, though advance credentials show evidence of ability and suitability for a position. How can you expect to make a good impression if you appear at the office door fifteen to fifty minutes late for a 10 A.M. appointment, with a heavy veil draped over a face well hidden by your picture hat, lipstick aglow, and offer some hazy excuse about having missed the train, despite the fact that you left home without the usual cup of coffee? The case is scarcely exaggerated; it is a composite description of the average applicant.

Seeking confirmation of, or disagreement with, my point of view, changed considerably by some six years of experience within earshot of management and personnel problems in a large research group, I went to New York recently to have a talk with Miss Doris Eager, manager of the Chemists' Club Bureau of Employment. Her background includes a college major in chemistry and long experience in personnel work. We discussed the various angles of the woman chemist's past, present, and future for more than two hours, and I cannot think of a single point on which we disagreed. We feel that a four years' course in the liberal arts colleges gives a good fundamental knowledge of chemistry, but fails to give adequate training in secondary but essential subjects, such as the supporting sciences, physics, biology, etc., languages, literature searching, an introduction to industrial chemistry, and last but not least, economics and business subjects, including shorthand and typewriting. Certainly under normal conditions, and (if you cannot now resist the urgent calls to an immediate position) later when the stress of war conditions has abated, a year spent in graduate study, preferably in a university with a well-recognized chemistry department, will prove well worth while. If the faculty of the women's colleges have failed in any respect to make the most of their opportunity, it is in a tendency to pamper their girls, overlooking what Dr. Roger Adams has called the most important item in the training of students, development of a good personality. Lack of self-confidence is an outstanding handicap not only in a personal interview but when undertaking any new problem. On the other hand, too much assurance may cover up inadequacies of training and ability which are sure to be revealed when work is started, and bring about a quick day of reckoning.

Present salaries are abnormal and uneven in scale, a direct result of war conditions and the sudden shift in personnel requirements. The woman who is seeking her first position will be wise to consider the type of work, the stability of the position, and the opportunity to gain valuable experience, rather than the initial salary. Routine positions in primary war industries no doubt offer most attractive remuneration, but they afford little opportunity to learn more chemistry of the usual industrial variety, and general working conditions are likely to be highly unsatisfactory. The woman intent on a real career in chemical industry will do well to choose an essential civilian rather than a war activity—for example, soap, textile, food, pharmaceutical manufacturing, or even one of the luxury fields, with the idea that those are the fields the "drafted" men will be forced to leave.

One would be bold indeed to try at this time to predict after-the-war conditions in all industry, and specifically whether women now entering hitherto closed portals will be able to hold their advantage. World conditions are too chaotic, and the time element too uncertain, to make positive statements regarding what the future may hold as a chemical career for women who are now preparing for their life work. It is true that the tenure of women in industrial chemical positions ceased abruptly after the close of the first World War. But economic conditions were then such that experienced men, who had given generously of their efforts in chemical war work, found it difficult to gain a foothold in civilian activities. By the time the prosperous era of the late 1920's arrived, and the infant American chemical industy was well on its feet, with but a few exceptions the woman chemist had disappeared from the industrial field. As to how many of these fell by the wayside, and how many took the matrimonial path out, there are no available records to consult. Times have not changed the handicap which all employed women face because of the well-established probability that a sudden romance will sooner or later bring about an equally sudden departure from the scene, despite promotions or any other inducement the employer may offer. Man's absentmindedness and distraction from his work while under the unusual emotional stress of his approaching marriage are overlooked and condoned because his superior knows his condition is temporary. Furthermore, the increased responsibility he has assumed will eventually induce greater effort to succeed and win promotion in his work. On the other hand, the woman, if she continues on the job at all, will have a division of interests. This fundamental difference makes the employment of women in any sustained operation where potential value grows slowly as a result of long experience a short term gamble instead of a sound investment. It explains both the differential in starting salaries and the unfavorable statistics regarding earning power over a long period of women in scientific work.

If the outcome of the war is what we all hope and believe it must be, there will be not only astonishing new developments in chemical lines, but a tremendous industrial activity to furnish replacements for consumer goods now completely shut off. Moreover, we shall have assumed an obligation to rehabilitate a devastated world, and that means food and clothing and innumerable supplies which must have chemical raw materials for their production. It appears entirely probable that the requirements for chemical personnel will be sufficiently great to take up the men released from war work and at the same time retain those women who have proved their ability. Competition will be keener, and you will have to give your best to survive.

Refrigeration

WARD V. EVANS *Northwestern University, Evanston, Illinois*

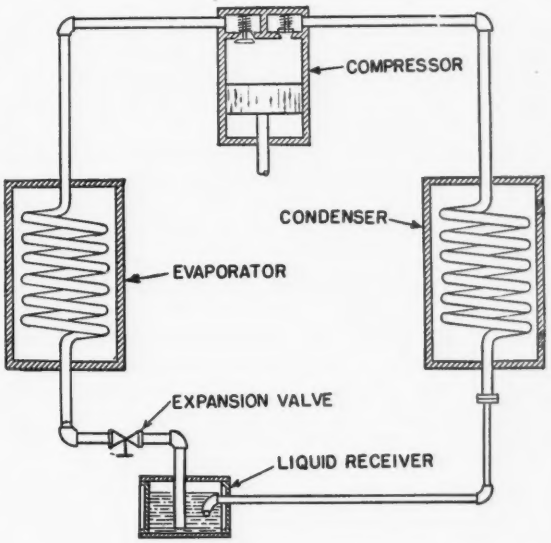
HISTORY OF REFRIGERATION

REFRIGERATION is the process of removing heat from an enclosed space that is to be maintained at a lower temperature than the surroundings. Producing a temperature lower than the surroundings by the use of substances capable of absorbing heat at temperatures below the temperature of the atmosphere has been practiced for centuries. Egyptian frescoes indicate that cooling water in a porous jug by fanning the jug was practiced as early as 2500 B.C. This method of refrigeration is still in use. In certain dry countries drinking water is cooled in an unglazed jug called in some localities a "monkey jug." The water seeps through the pores in the jug and evaporates on the surface into the dry air. The evaporation, and hence the cooling, can be hastened by swinging or fanning the jug or by a gentle breeze. If the air surrounding the jug is very dry, it is possible to keep drinking water cool all day by this process.

Although it may seem remarkable to keep water cool on a hot day by this simple method, it is still more remarkable that the water can be cooled in this way much below the temperature at which it was placed in the jug. Parks, in his book, "Wandering of a Pilgrim," states that it was the custom in certain regions along the Indus to manufacture ice by rapid evaporation of water into the atmosphere during the night. The water was placed in shallow pans insulated from the hot earth by a thick layer of straw and with night-air temperatures as high as 40°F. it was possible to freeze ice from 1 to $1^1/_2$ inches thick before sunrise the next morning. Of course, the air must be very dry and there must be considerable radiation of heat into a cloudless sky in order to get freezing temperature at the surface of the water. The appearance of what is called a "white" frost early in the fall on a clear, cloudless night when the air is very dry and the temperature about 32°F. is due to exactly the same process.

Another early method of refrigeration was to put food and water into caves. In nearly all countries there are artificial caves, cellars, and wells in which a temperature between 50° and 60°F. may be maintained even in warm weather. Many of the early homes on our Atlantic seaboard were equipped with a vault underground, and frequently connected with the well, where meat and milk could be kept at a temperature not exceeding 60°F.

The ice box using natural ice came into use early in the 19th century. Natural ice was probably first used in 1802, and a few years later natural ice was shipped from Boston to the West Indies. Today artificial ice has very largely replaced natural ice.



The Elementary Refrigeration Cycle.

THEORY OF REFRIGERATION

These oldest known examples of refrigeration made use of exactly the same physical principles as are employed in our most modern mechanical refrigeration. The only difference is that in our modern refrigeration we have developed better and more suitable substances than ice and water for producing low temperatures. We have also perfected elaborate machines for utilizing this age-old principle used in refrigeration. It might be well for us to consider just what this principle is and why it works.

When a substance changes its state, heat is either absorbed or liberated. Thus, when a substance such as ice melts, it absorbs a certain amount of heat. Since heat is a form of energy, this heat energy disappears and reappears as molecular motion in the liquid state of the substance. Since water has more molecular motion than ice, it contains more energy than ice, and it takes eighty calories of heat to change one gram of ice into one gram of water at exactly the same temperature. This temperature with ice is 32°F., or 0°C. Likewise, when a substance such as water changes into water vapor, a large amount of heat energy is utilized in separating the molecules from each other. This amount of heat energy is 536 calories of heat for each gram of water converted into vapor. When this process takes place at atmospheric pressure, the tempera-

ture of the transformation is 100°C., or the boiling point of water at one atmosphere of pressure.

But water can be made to boil at a much lower temperature than 100°C. by reducing the pressure upon it with a vacuum pump. Thus, at one-half an atmosphere water will boil and change to a vapor at about 82°C., and at one-tenth of an atmosphere of pressure this change takes place at 46°C., while if we reduce the pressure to about 7.6 mm. of mercury, or $^1/_{100}$ of an atmosphere, the boiling point of the water would be 7°C. This is about 44°F., much too low a temperature to go bathing, yet the water is "boiling hot."

If we had a good vacuum pump and reduced the pressure on the water to 4.57 mm. of mercury or to about $^1/_{167}$ of an atmosphere, the water would boil at 0.007°C. This temperature is the boiling point of water under its own vapor pressure, and is also the freezing point of water under its own vapor pressure. Now, under the conditions we have stated, that is, $^1/_{167}$ of an atmosphere of pressure and at a temperature slightly greater than 0°C., we can have boiling water, freezing water, and ice all together in any quantity we desire. This temperature and pressure we call the equilibrium conditions of ice, water, and water vapor, and we cannot change either the temperature or the pressure on this system as long as all three (ice, water, and water vapor) are present. If we try to heat the system, ice will melt and absorb the heat we add. If we try to cool the system, water will freeze and add to the system the heat we are taking out. If we attempt to increase the vapor pressure, vapor will condense and thus keep the pressure constant. If we try to evacuate our system to a lower pressure, water will evaporate and keep the pressure constant.

When water changes to vapor at a temperature lower than its boiling point, it still absorbs approximately the same number of calories, namely 536 calories, and likewise gives up this number of calories when the vapor changes to a liquid. Since the boiling point of water and its vapor pressure are so linked together, if we attempt to boil water at a very reduced pressure, the temperature of the water must fall until we reach the equilibrium temperature and pressure. We see from this principle that if water evaporates into a near vacuum the temperature of the container and the water must fall, and any substances surrounding this container will be reduced in temperature. Thus, the evaporation of water at a low pressure could be used as a refrigerating medium just as the melting of ice could be thus used.

Since water and ice together are in equilibrium at 0°C. under a pressure of one atmosphere, we might ask ourselves what would happen if we added a soluble substance such as salt to this mixture. The answer is, the temperature would fall below zero, and the drop in temperature would depend upon how much salt we added, provided we also kept ice present. If we added more salt than the water could dissolve, we would have an equilibrium mixture of ice, water, and salt, and the temperature would be −21°C. This is the strongest brine solution we could make, and the lowest temperature we could produce with a brine solution containing ice. Solutions such as this have great use in refrigeration.

The behavior of systems such as we have described is often puzzling to laymen but the facts are apparent to all of us. It is only the explanation of these facts that is difficult. Let us suppose that we have a glass of ice and water on a table. If we have considerable ice in the water, the temperature of the mixture will be almost 0°C. on the hottest day. Now we add salt, and the salt is at room temperature. If a thermometer is placed in the glass, we see that the temperature of the salt solution is falling in the warm room, and the ice is melting very rapidly. By adding more salt and replenishing the supply of ice we can obtain a brine solution with a temperature more than 20° below the freezing point of water.

Another application of this same principle is sprinkling salt on the sidewalk to melt ice even when the temperature of the surrounding air is at the freezing point. When students are asked why warm salt makes the ice melt, they seldom give a correct answer. The freezing point of water is 0°C., and this is the temperature at which ice, water, and water vapor are in equilibrium *under atmospheric pressure.* The vapor pressure of water at this temperature is 4.57 mm. of mercury, and the vapor pressure of ice is the same. The temperature of the mixture is 0°C. If the temperature of the air is also 0°C., we have the equilibrium state. If the temperature of the air is above zero, ice will melt and absorb heat to maintain the 0° temperature until the ice is all melted. If the air temperature is below 0°, water will freeze and throw out heat until the water is all frozen.

When we sprinkle salt on the ice on the sidewalk the salt takes some water from the air and dissolves in this, forming a solution, but it does not dissolve in the ice. Since solution of a solid in a liquid lowers the vapor pressure of the liquid, the vapor pressure of the system becomes lower than 4.57 mm., and since ice cannot exist in equilibrium with a solution at 0°C. but can exist at some lower temperature where its vapor pressure is lower, ice begins to melt; this takes heat and the temperature of the solution falls to a new lower temperature where ice solution and vapor can again be in equilibrium.

If the outside temperature is above the freezing point of water, and if we add lots of salt to make a strong solution that could be in equilibrium only at a very low temperature, say −15°C., the ice will melt very quickly. However, if the temperature were −22°C. the ice and salt would exist together and no melting would occur. Thus the change in the temperature of the freezing point of a solution is a very characteristic phenomenon and depends, at constant pressure, only on the concentration of the solution. This is rather analogous to the change in the boiling point of a pure solvent with pressure.

Although the change in the boiling point of a pure substance with pressure is very great, the freezing point of a pure substance changes little with pressure. It takes 130 atmospheres of pressure to lower the freezing point of ice one degree. Thus, if we had snow which would be at 0°C. provided the outside temperature was above zero, and we attempted to make a snowball, a very little pressure with the hands would cause part of the snow to melt because pressure lowers its melting point slightly. As soon as we relieve the pressure the water freezes again and we have made what used to be called a "water soaker." However, if the temperature was 1° below freezing, it would take more than 130 atmospheres of pressure to make the same kind of snowball.

What has been said about the changes of state in ice and water could equally well be said of any other substance. Any substance that changes its state can be used for producing low temperatures, and our business is to select the most suitable substance for refrigeration.

Refrigeration in its earliest form, of course, was concerned with the change in state of water and ice. The absorption of heat by the melting of a solid is shown by the cooling of the air caused by the melting of snow on an ice-capped mountain, or the freezing of ice cream by melting ice outside the ice cream can.

This melting of ice is a *cooling process* and the freezing of ice is a *warming process*. Vegetables and canned fruit can be kept from freezing in a cellar by putting tubs of water in the cellar. The ice freezes at 0°C. and throws out heat that keeps the vegetables warm and prevents freezing, since their freezing point (due to the salts and sugars dissolved in their solutions) is below 0°C.

MECHANICAL REFRIGERATION

The cooling effects of allowing ether to evaporate from the palm of the hand or of taking an alcohol sponge bath are well known and those phenomena are based on this same familiar principle: absorption of heat due to the evaporation of a volatile liquid at some partial pressure much below atmospheric, where the temperature at which heat is absorbed is corresponding to the partial pressure of the volatile liquid. The fact that in winter a humid atmosphere makes a room feel warmer, and a dry atmosphere makes it feel colder than it really is, is due to the same refrigeration principle.

Water has too high a boiling point and too low a vapor pressure to work well as a refrigerant in the open air, and if such substances as alcohol or ether were evaporated in the open and the vapor escaped, the process would be too expensive. We can freeze water and make ice in the hottest climate by allowing ether to evaporate from the water container, but the cost of the ether would be enormous compared to the value of the ice. It would be like cutting up the grand piano to get kindling to start a fire. If the vapor could be saved and used over again, we could utilize this principle. To save this vapor, evaporation would have to take place within a closed space such as a pipe system. Means would have to be provided for returning this vapor to the liquid state. A pump run by a motor or an engine would do this. The accompanying diagram will explain this simple process.

The refrigerant is contained in the liquid receiver. From here it travels through a pipe to an expansion valve. It squirts through this valve into a coiled pipe that is connected to a compressor. This pipe is kept under reduced pressure. Here the liquid evaporates and produces a low temperature in the coil. The vapor is then passed into the compressor at its low temperature and here work is done on the vapor and it is compressed. During this compression it gets hot. The warm vapor is next led into another coil where it is cooled to room temperature and condensed to a liquid. From here it goes back to the liquid reservoir to be used over again.

The motor which runs the compressor is the mechanical agent used to liquefy the vapor of the refrigerant. In reality this motor is pumping heat out of one side of the system at a low temperature and discharging it to the outside air at a higher temperature. The liquid refrigerant is simply the conveyor to carry the heat out.

The evaporator is in contact with the material we wish to refrigerate, and the condenser is either on the top of the refrigerator or in some other locality where its heat can be dissipated. Various forms of this simple diagram make up the modern refrigerator. In some types of machines, in order to avoid moving parts that necessitate lubrication, an absorption system is used. Here the refrigerant is absorbed in water and driven out again and vaporized by a gas flame which works intermittently. The energy is supplied by the flame rather than a motor.

Artificial refrigeration in transportation, in storage, in the home, and in air conditioning is an achievement deserving the highest commendation. The greatest advances in this art have occurred in the past twenty years. It is only recently that substances other than carbon dioxide, cold brine, or ammonia have come into use as refrigerants. With the advent of the household machine a demand has arisen for other refrigerants that would have suitable characteristics to render them applicable to small machines. The resources of our industries have been taxed to find substances with suitable properties and suitable boiling points so that they could be liquefied and evaporated without the use of great pressure or vacuum.

In our selection of a suitable refrigerating agent, unfortunately, there are many more things to consider than suitable boiling point. There are certain inherent hazards in the use of refrigerants. These hazards can be fairly well controlled in industrial refrigeration because suitable precautions can be enforced. In household refrigeration, however, the control of these hazards is more difficult. The refrigerating machinery has to be lighter and substances with different properties have to be used. Reviewing the history of mechanical refrigeration we find that more than fifty different substances or mixtures have been used in compression and

absorption machines. Table 1 gives a list of some of these substances and other substances that might be used.

TABLE 1

SUBSTANCES THAT MAY BE USED AS REFRIGERATING MEDIUMS*

Glycerin	Dichlor methyl ether
Pentachlorbenzene	Heptane
Trichlorbenzene	Ethylene trichloride
Ethylene-glycol	Hydrogen sulfide
Methyl aniline	Trimethylene
Aniline	Methyl ether
Phenol	Methylamine
Dichlorbenzene	Trimethylamine
Decane	Dimethylamine
Chlorpyridine	Methyl ethyl ether
Chlortoluene	Ethyl ether
Pentachlorethane	Dichlormethane
Nonane	Carbon disulfide
Acetylene tetrachloride	Diethylamine
Xylene	Acetone
Amyl alcohol	Methyl alcohol
Chlorobenzene	Hexane
Octane	Carbon tetrachloride
Tetrachlorethylene	Ethyl alcohol
Butyl alcohol	Benzene
Pyridine	Propyl alcohol
Toluene	Triethylamine

* TAYLOR, "Heat operated refrigerating machines of the absorption type," *Refrig. Eng.*, **17**, 136 (1929).

Most of the substances named in this table, however, are unsuitable for household refrigerants. Their physical constants are such that special machinery would be required to make available their heat of vaporization.

Table 2 includes a list of present-day refrigerants.

TABLE 2

Refrigerant	*Symbol*
Carbon dioxide	CO_2
Ethane	C_2H_6
°Ammonia	NH_3
°Propane	C_3H_8
°Methyl chloride	CH_3Cl
°Sulfur dioxide	SO_2
°Isobutane	C_4H_{10}
°Butane	C_4H_{10}
°Ethyl chloride	C_2H_5Cl
Dichloromethane	CH_2Cl_2
Dichloroethylene	$C_2H_2Cl_2$
Trichloroethylene	C_2HCl_3
°Dichlorodifluoromethane	CCl_2F_2
Dichlorotetrafluoroethane	$C_2Cl_2F_4$
Dichloromonofluoromethane	$CHCl_2F$
Trichloromonofluoromethane	CCl_3F

Those refrigerants marked with a circle (°) are used chiefly in small household units. The others have properties, such as boiling points, that make them suitable for large refrigerating machines and they find their use in cold storage, ice making, and air conditioning.

Perhaps a special word should be said about the last four refrigerants called the "Freon" group of refrigerants. This group of refrigerants was made synthetically, bearing in mind just what the properties of an ideal refrigerant should be.

Since the application of chemical refrigerants (that is, refrigerants other than ice, water, and air) to many industrial and domestic uses, considerable thought had to be given to the types of chemicals we introduce into our homes and factories. All the refrigerants in common use are toxic substances, or at least substances dangerous in large quantity; if they escape from the refrigerator they are a serious menace. The regulation of these refrigerants became a health problem of the first magnitude. Before the advent of the small machine, the specifications for a refrigerant dealt only with its physical characteristics. Today the chemical and physiological properties are just as important. Also, their cost of production must be considered.

Now, what are the characteristics of a liquid that would be an ideal refrigerant?

1. It must be non-corrosive. That is, it must not act in any way on its metal container.
2. It should be non-toxic. If the refrigerator springs a leak and the refrigerant escapes into the home, there should be no health hazard.
3. It should be non-inflammable and not a fire hazard under any circumstances.
4. It should be non-explosive. In case of a leak, when the substance escapes and mixes with air in the presence of an open flame, there should be no possibility of an explosion.
5. Its boiling point must be such that it can be liquefied and vaporized without the use of great pressure or excessive vacuum. In either of these cases heavy machinery would have to be employed.
6. It should have as large a heat of vaporization as possible, to assure its efficiency as a refrigerant.
7. It should have a characteristic odor, and thus furnish a warning when a leak occurs in the system.
8. It should lend itself readily to the detection of leaks.
9. It should be stable under heat and pressure and not decompose into other substances.
10. It should be incapable of forming toxic or obnoxious substances if exposed to flame.
11. It should have a low cost of production.

We have here a list of chemical and physiological characteristics for the ideal refrigerant to approach. Since no known substance at present fulfils all these requirements, we can safely say that the ideal refrigerant is purely imaginary. If we attempt to note the chemical substances that can be used as refrigerants, we find that they all fail in at least one particular. They are all toxic and cause discomfort and even death if in sufficient concentration. Even carbon dioxide is harmful in sufficient concentration, if for no other reason than cutting down the oxygen supply. Air and water are not suitable for use because of improper boiling points which require excessive pressure on the one hand to cause liquefaction, and high vacuum on the other to cause vaporization.

We can construct a table of the substances whose boiling points and critical temperatures enable them to be used easily as refrigerants in household units, and state the qualifications we have outlined. We will have seven substances in our table. We may arrange the table and rate our refrigerants from one to seven in regard to certain characteristics (Table 3). We note that none of our common refrigerants has a perfect rating. The best rating is for the youngest refrigerant in the group and one that was made especially for the use to which it is put.

Ammonia is used and undoubtedly will continue to be used extensively in the United States in commercial refrigeration, although the Freon refrigerants are being adopted in new installations. Ammonia is dangerous

to animal life and corrodes copper. It has a large heat of evaporation, and its physical properties adapt it to economical use. Leaks are also easily detected. Carbon dioxide has been used as a "safety" refrigerant for a long time. Its presence in the hold of a ship, even in a large per cent by volume, is not a serious hazard unless the exposure is prolonged. The pressure required to condense it to a liquid, however, is excessive for condenser water at 70°F. With cooling water above 80°F., it will not condense and operate efficiently. It is not suitable for the household unit. Sulfur dioxide is used very widely in small refrigerators, although its place is now being taken by Freon 12 or dichlorodifluoromethane. Sulfur dioxide is not inflammable, but it is an irritating, toxic gas. It gives warning with its odor, however, and is practically harmless in small household units, owing to the small quantity used. However, it is dangerous in multiple systems. It must contain no water, otherwise it corrodes metals. Freon 12 is taking the place of both ammonia and carbon dioxide, especially where the public is exposed seriously to heavy leaks. It is almost an ideal refrigerant, inasmuch as it is not toxic, inflammable, or irritating. The air-cooled condenser can be used, and leaks are easily detected.

The absorption machine was more important a few years ago than today. This machine requires the direct application of heat instead of mechanical work in order to increase the pressure of the gas to a point where liquefaction may occur in the condenser. The heat necessary for this action may come from a gas flame or from exhaust steam. The principle of the action of the absorption machine is that a solution of ammonia and water is used in a still to which heat is applied. The heat drives out some of the gas from the solution. This gas passes to a condenser—kept at low pressure—where it liquefies. The liquid then passes to the evaporator in the same manner as in the case of the compressor system.

However, the gas from the evaporator has to be returned as a solution of strong ammonia to the generator or still. This is done by cooling the weak ammonia solution which was left in the still after heating, and sending it to an absorber where it is brought into contact with the gas from the evaporator. The resulting strong solution occupies a small volume in comparison to that of the gas, so that the ammonia has been "condensed" as though by a compressor. The solution is then pumped back into the still where it is heated again. The advantages of the absorption machine are the use of exhaust steam and low cost. This type of machine is used in packing plants, oil refineries, and some hotels. This machine has one moving part, the pump.

In the intermittent absorption machine the still or generator is also used as an absorber. During the period when the heat is applied to the generator, the ammonia gas distils off to the condenser to be condensed, and is finally stored in a liquid receiver. When the required amount of liquid has accumulated, the steam or gas is shut off, cooling water is turned on, and the expansion valve opens. As the liquid passes into the evaporating coils refrigeration is accomplished and the gas proceeds to the generator, now acting as an absorber, and is kept cool by water cooling coils. This machine, of course, cannot give continuous refrigeration, but it acts automatically. There is another type of absorption machine, however, that is automatic, continuous, and has no moving parts.

The small household refrigerator did not become popular until it was made automatic. The electrically driven household unit and the gas flame unit have become highly reliable. They have a means of starting and stopping dependent on the box temperature. The modern automatic machine can be set to maintain within a few degrees any desired temperature within the usual operating limits. The assembly has been perfected against leaks of oil and refrigerant so that at present the original charge under ordinary conditions will last for years and servicing the unit be reduced to a minimum.

APPLICATIONS OF REFRIGERATION

The applications of refrigeration at present are very numerous. They include (1) cold storage, (2) packing plants, (3) marine refrigeration, (4) ice making, (5) comfort cooling or air conditioning, (6) district cooling.

By *cold storage* the season for fruits and vegetables is increased from a few weeks to six months. Eggs can be kept from the period of great plenty in the spring until fall, and modern meat packing could not exist without refrigeration.

Marine refrigeration requires four types of refrigerator equipment. (1) Fruit carriers require forced circulation of cool air. (2) Frozen meats require no air circulation but do require good insulation and low storage temperature, from 12° to 15°F. (3) Chilled meats require heavy brine piping, with the pipes located under the ceiling. The temperature of the cold storage room must be controlled within a small temperature difference. (4) Where general cargoes are carried the frozen meats may be carried in the lower holds.

TABLE 3

	Ammonia	*Butane*	*Carbon Dioxide*	*Ethyl Chloride*	*Methyl Chloride*	*Sulfur Dioxide*	*Dichlorodifluoromethane*
Immediate toxic effects	6	1	2	3	5	7	1
Delayed toxic effects	1	1	1	1	7	1	1
Flammability	4	7	1	6	5	1	1
Efficiency	2	5	6	2	4	1	3
Pressure developed	6	2	7	1	4	3	5
	19	16	17	13	25	13	11

See *J. Am. Med. Assoc.*, **94**, 1832–8, 1842, and 1843 (1930).

District cooling. Certain cities and towns find it convenient to have a central cold storage plant which will supply refrigeration under contract.

Ice making is, of course, important and was an industry with more than a billion dollar investment in 1924. The household machine has cut down on this business, yet the manufactured ice industry has increased 10 per cent annually. The natural ice trade is now almost negligible.

Comfort cooling, one of the important applications of *air conditioning,* is the outstanding development of refrigeration. It has made possible the use of auditoriums in the summer with the same degree of comfort in temperature, humidity, and air movement as at other periods of the year. It is not required that the temperature be reduced much below that of the outside air, but the humidity must be low enough to prevent uncomforable conditions due to moist clothing and skin. As a general statement, the relative humidity must be from 40 to 50 per cent and the temperature from 5 to 10°F. below atmosphere. The movement of the air must be positive without causing drafts, and the air must be washed and filtered enough to prevent odors. The usual method of securing comfort cooled conditions involves the use of cool water either in a spray or inside pipes or tubes which have extended surfaces. In either case the air to be cooled is brought into contact with the water which washes it, and the air temperature is reduced enough below the dew point for the water vapor remaining in the air to be of the proper amount.

Refrigeration is at present in its infancy. In the years to come we shall likely see great advances made, particularly in living comfort.

BIBLIOGRAPHY

EVANS, *Trans. Nat. Safety Congress,* **1,** 482–7 (1931).
J. Ind. Eng. Chem., **24,** 620 (1932); *ibid.,* **22,** 542 (1930).
MACINTIRE, "Refrigeration engineering," 2nd ed., Wiley and Sons, New York, 1940.
THOMPSON, "Properties and characteristics of refrigerants" (Lecture before the Refrigerating Service Engineering Society).

Division of Chemical Education

OF THE AMERICAN CHEMICAL SOCIETY

MINUTES OF THE EXECUTIVE COMMITTEE MEETING

Buffalo, September 8, 1942

A MEETING of the Executive Committee was held in Townsend Hall, University of Buffalo, Tuesday, September 8, 1942, at 5:00 P.M. Those present were: F. E. Brown, Chairman, A. J. Currier, R. D. Reed, C. E. White, L. L. Quill, N. W. Rakestraw, P. H. Fall.

Minutes of the Executive Committee at the Memphis meeting were read.

The chairman reported that he had heard numerous complimentary remarks concerning the Symposium on Teaching and Practice of Analytical Chemistry, which was held jointly with the Division of Analytical and Micro Chemistry at the Tuesday morning session.

O. M. Smith, Chairman of the Committee on Examinations and Tests, present by invitation, reported that his committee had held a conference in Buffalo for two and a half days immediately preceding the meeting of the American Chemical Society. At his suggestion, and because the committee is expanding its activities, it was voted that the committee be enlarged by the addition of three men. Thereupon the chairman named as the three new members of the committee: Frank D. Martin, of Purdue University; J. S. Coles, of Middlebury College, and Alexander Calandra, of Brooklyn College. The chairman also reappointed to the committee the two men whose terms expired in September, 1942: Ed. F. Degering, of Purdue, and Earl W. Phelan, of Georgia State Woman's College.

This important Committee on Examinations and Tests is now constituted as follows:

O. M. Smith, Chairman, Oklahoma A. and M. College.

Term expiring September, 1943: B. C. Hendricks, University of Nebraska; R. D. Reed, New Jersey State Teachers College; Frank D. Martin, Purdue University.

Term expiring September, 1944: T. A. Ashford, University of Chicago; L. S. Foster, Brown University; J. S. Coles, Middlebury College.

Term expiring September, 1945: Ed. F. Degering, Purdue University; E. W. Phelan, Georgia State Woman's College; Alexander Calandra, Brooklyn College.

Motion was made and carried that O. M. Smith, Chairman of the Committee on Examinations and Tests, be authorized to confer informally with the Council Committee on Professional Training of American Chemists as to possible service which his committee may render the above-named accrediting committee.

By letter, M. V. McGill, Chairman of the Committee on High School Chemistry, recommended that the three members of his committee whose terms expire September, 1942, be reappointed. Subsequently, the Chairman of the Division, in accordance with this request, named Elbert C. Weaver, Robert L. Ebel, and Harold W. Baker to succeed themselves. This Committee on High School Chemistry is now constituted as follows:

M. V. McGill, Chairman, Lorain High School, Lorain, Ohio.

Term expiring September, 1943: T. A. Nelson, Decatur High School, Decatur, Illinois; R. D. Reed, State Teachers College, Montclair, New Jersey; Ernestine M. J. Long, Normandie High School, St. Louis, Missouri.

Term expiring September, 1944: T. A. Ashford, University of Chicago; T. D. Kelsey, Grover Cleveland High School, St. Louis, Missouri.

Term expiring September, 1945: Elbert C. Weaver, Bulkeley High School, Hartford, Connecticut; Robert L. Ebel, Edison Institute, Dearborn, Michigan; Harold W. Baker, James Ford Rhodes High School, Cleveland, Ohio.

The chairman reported that as yet no one had been named to the Committee to Study Problems of Technical and Non-Collegiate Chemistry, nor to the Committee to Study Problems of Teachers of Chemistry in Colleges and Universities. Both of these committees were created at the Atlantic City meeting.

A suggestion was made that we have reports of committees as part of our regular divisional programs, but no definite action was taken, since it was felt that this might not be entirely satisfactory.

Dr. J. C. Bailar of the University of Illinois, was elected to the Board of Publication of the JOURNAL OF CHEMICAL EDUCATION for the three-year period ending September, 1945, succeeding N. D. Cheronis, whose term expired in September, 1942. Likewise, Dr. W. L. Evans of Ohio State University was made a member for a two-year term ending September, 1944, thus succeeding Dr. R. A. Baker, whose term had continued an extra year.

The present members of the Board of Publication, with their terms of office, are as follows:

S. R. Brinkley, Chairman, Yale University, to 1943; W. L. Evans, Ohio State University, to 1944; J. C. Bailar, University of Illinois, to 1945; A. J. Currier, Pennsylvania State College, to 1943; P. H. Fall, Secretary, Hiram College, to 1943; N. W. Rakestraw, Editor of the JOURNAL OF CHEMICAL EDUCATION, to 1945.

Treasurer C. E. White presented a report which was accepted. The Chairman appointed L. L. Quill to audit the Treasurer's accounts. The report, subsequently audited and found correct, is appended.

Motion was made and carried that the Treasurer be instructed to invest $300 of our Savings Funds in U. S. Government (War) Bonds in units of $50.

—PAUL H. FALL, *Secretary*

TREASURER'S REPORT

Receipts

Received from Dr. V. Bartow, retiring treasurer	$363.82	
Received from Mr. Martin McGill on Supp. Expts.	35.00	
Received from dues	142.00	
Total receipts		$540.82

Disbursements

Stamps, Feb. 25, 1942	$14.50	
Envelopes, Mar. 4, 1942	2.50	
Secretary's Office, P. H. Fall, Apr. 24, 1942	25.00	
Am. Science Teachers Assoc., Apr. 24, 1942	5.00	
Abstracts for Memphis Meeting, May 11, 1942.	10.18	
Total disbursements		$57.18
Credit Balance		$483.64
Savings Account P. G. Bank & Trust Co., Hyattsville, Maryland		$360.00
Checking Account P. G. Bank & Trust Co., Hyattsville, Maryland		121.64
Cash on hand		2.00
		$483.64

C. E. WHITE, *Treasurer*

MINUTES OF THE BUSINESS MEETING

Buffalo, September 9, 1942

The business meeting of the division was held at 11:30 A.M. Wednesday, September 9, in Townsend Hall, University of Buffalo, at the close of the divisional program.

By motion, the report of the business meeting at Atlantic City in September, 1941, was accepted as printed in and circulated by the JOURNAL OF CHEMICAL EDUCATION (**18**, 532 (1941)).

The Secretary reported the action taken by the Executive Committee at its meeting the preceding day. (*q. v.*)

Dr. S. R. Brinkley, newly elected chairman of the Board of Publication of the JOURNAL OF CHEMICAL EDUCATION, reported that Dr. N. W. Rakestraw had been re-elected Editor of the JOURNAL for the three-year period ending September, 1945.

Dr. O. M. Smith, Chairman of the Committee on Examinations and Tests, reported that about forty people had attended the two and a half-day conference on Examinations and Tests held in Buffalo immediately preceding the Society meeting. He stated that his committee had decided to use the 1942 Form in General Chemistry in the 1943 Testing Program and that the committee is constructing a battery of standardized tests covering the major fields of the elementary chemistry curriculum. This involves tests not only in General Chemistry, but also in Qualitative Analysis, Quantitative Analysis, Physical Chemistry, and Organic Chemistry.

The Nominating Committee, consisting of R. A. Baker, Chairman, Ed. F. Degering, and O. M. Smith, presented the following nominees for officers for the year September, 1942, to September, 1943:

A. J. Currier, Chairman, Pennsylvania State College
L. L. Quill, Vice Chairman, University of Kentucky
C. E. White, Treasurer (for a 3-year period ending September, 1945)
H. N. Alyea, Member-at-Large, Princeton University

These were elected by unanimous vote cast by the secretary.

The above four, with the Immediate Past Chairman, F. E. Brown of Iowa State College, and the Secretary, P. H. Fall of Hiram College, constitute the Executive Committee for the current year ending September, 1943.

PAUL H. FALL, *Secretary*

Out of the Editor's Basket

E. E. JOHNSON, of Omaha, Nebraska, reports that a modified form of an apparatus for microsublimation, microdistillation, and gas evolution may be constructed from a broken porcelain spatula, a Stoddard test tube clamp, and a microscopic slide. The arrangement of the parts is shown in the diagram.

● A new type of opaque glass that floats like cork and can be used as the buoyant element in the construction of life boats, life rafts, life preservers, and pontoon bridge supports has been developed by the Pittsburgh Corning Corporation.

The new product, called Foamglas, also has valuable insulating qualities. It has a weight of only ten pounds per cubic foot—one-fifteenth that of ordinary glass—and is odorless, fireproof, and vermin-proof.

It is now under active investigation by certain Federal Government Agencies as an alternate material for such critical products as cork, balsa wood, cellular rubber, and kapok, which are largely imported.

Foamglas is produced by firing ordinary glass which has been mixed with a small quantity of pure carbon. At the proper temperature the glass softens and the carbon burns to form a gas which then acts upon the molten glass very much as baking powder or yeast behaves when bread is baked. By proper selection of the glass batch, the type of carbon, and by exact control over the times and temperatures used, it is possible to obtain rigid vitreous slabs of Foamglas in which the cells are uniformly small in size and entirely separate.

● It has always been difficult to argue the dollars-and-cents value of industrial research. Eugene Ayres, of the Gulf Research and Development Company of Pittsburgh, recently presented a paper before the American Chemical Society based upon a careful statistical analysis in which he gave a tabulation showing units of cost in three generalized cases, based on averages, for the following stages of research: laboratory research, pilot plant research, excess design and construction, and "getting process in operation."

He said that the generalized figures point toward some interesting conclusions, as follows:

1. Patent prosecution and laboratory research are almost negligible portions of total development expense.
2. Total research, including adequate pilot plant work under the most favorable conditions, figures around one-fifth of the total development expense.
3. The minimum development expense is associated with adequate research expenditures.
4. Research is about the most profitable investment that can be made.

One company found it necessary to go into the manufacture of a new chemical in a hurry. There were no large-scale precedents for this operation, but two good process ideas were offered by the research department. Because of the emergency, it was decided to commercialize one idea without any research, while the second idea was carried in orderly fashion through laboratory and pilot plant. Despite the delay occasioned by months of research, the second idea resulted in a smoothly operating plant before the first, and at much lower development cost. The first idea was then sent back to the research laboratory, and a year later superseded the second.

In another case, a new process was commercialized from laboratory data without pilot plant research. A few years later, a new plant of the same size was designed and built from data secured from the first plant.

From these and dozens of other cases, it is possible to come to some general numerical conclusions.

	Units of Cost		
1. Laboratory Research	1	1	0
2. Patent Prosecution	1	1	0
3. Pilot Plant Research	5	0	0
4. Excess Design and Construction	5	15	20
5. Getting Process in Operation	25	50	65
Total Development Cost	37	67	85

The first column expresses the relationship between cost elements which perhaps may be regarded as ideal and, therefore, as showing a minimum total for the average research project. Laboratory research and patent prosecution are indicated as of the same order of magnitude. Pilot plant expense is five times as high as laboratory expense. "Excess Design and Construction" is made equal to pilot plant expense because experience indicates that this is about as low as competent research can bring it and "Getting Process in Operation" is five times as great for the same reason.

The most significant comparison is between the columns. Without any research, the total development cost is about 2.3 times the total cost with adequate research. Laboratory research without pilot plant work figures 1.8 times the ideal.

● Teachers and directors of small laboratories would be interested in an article in the September number of the *Science Counselor* of Duquesne University dealing with the various federal regulations controlling the purchase of science supplies. The article was written by E. S. Russel of Chembusco Scientific Company.

● Requests have been received by the Committee on the Location of New and Rare Instruments for a number of instruments from research workers who urgently need them. If you have any of them available to lend, lease, or sell, please write the chairman, D. H. Killeffer, 60 East 42nd Street, New York City.

INSTRUMENTS SOUGHT

Microammeters and electrical meters generally.
Ultra-violet microscope.
Zeiss Optimeter (for measuring fine wires to 0.00001-inch).
Two circle Reflecting Goniometer (Goldschmidt).
Electro-Encephalograph (3 channel).
Warburg Apparatus.

● To date over 14,000 firms have reported a total of 111,000,000 pounds of idle and excess inventories of copper and copper base alloys.

● Wood-and-glue's large part in the present conflict is confined not only to the prefabricated housing field, but is out in the line of fire in wood-and-glue airplanes, wood-and-glue ships, etc. Wood and glue are playing an equally important part in the construction of smaller items, such as the construction of laminated spars for minesweepers, laminated wood deck cleats, glued-up ammunition boxes, wood-and-glue Army desks, etc. Wood and glue are saving tons of steel for more important war uses when they build heavy construction members—laminated beams and arches to hold up armories, hangars, chapels, etc.

● Extracted soybean meal, furfural, phenol, and ammonium hydroxide when heated together form a resin which, mixed with hexamethylenetetramine and either wood flour or asbestos filler, produce a plastic of excellent strength and appearance.

Another plastic molding material is made from corncobs or oat hulls, cresol, and sulfuric acid, without the addition of fillers, and a similar product, with fillers, results in a thermoplastic molding powder. Furfural, hexamethylenetetramine, and filler added to this thermoplastic substance produce a thermosetting plastic.

Acid-hydrolyzed cornstalks and oat hulls mixed with furfural, aniline, filler, and in some cases other materials, can be molded into plastics of excellent strength, good appearance, and satisfactory absorption.

● Housed in a special building, with three-foot concrete walls, a machine which will speed electrons to energies of 100,000,000 volts, and which will produce X-rays of the same power, is being constructed as an addition to the General Electric Research Laboratory.

The machine about to be installed, called an "induction electron accelerator," will give electrons energies far higher than have ever been given by a human agency before. It will provide science with a new tool, the full capabilities of which will have to be explored. Its principle has been described before in this column.

One of the investigations with the equipment will be a determination of the maximum thickness to which X-rays can usefully be applied for examination of armor plate and other very thick cross sections. Eight inches of steel represents the practical limit for convenient use of the present million-volt industrial X-ray unit. Increased voltage, above a million, will increase the penetrating power of X-rays. Since the new accelerator will produce X-rays at any voltage to a hundred million it will be used to determine the useful limit.

LETTERS

Discovery of the Elements

To the Editor:

In 1939 Dr. George Sarton asked me to review for his journal, *Isis*, the then new (fourth) edition of Dr. Mary Elvira Weeks's "Discovery of the Elements," published by the JOURNAL OF CHEMICAL EDUCATION. *Isis*, at that time, was printed in Belgium, and so it came about that the appearance of the number containing my review was prevented by the German invasion. It has occurred to me that some of the points of my review might interest your readers. With Dr. Sarton's kind permission I accordingly quote as follows.

"Professor Weeks's book is noteworthy in that it unites two points of view seldom found united: on the one hand it conveys a real appreciation of the fact that chemistry is an expression of culture—in the same sense as are, say, medicine, music, or manners—and that the history of chemistry is therefore indissoluble from the history of culture as a whole; and on the other hand, by virtue of the descriptions, in some cases very detailed, of the experiments whereby the elements were discovered and first prepared in the free state, the book radiates the practical spirit of the chemical laboratory. Since in elementary instruction in chemistry there is at present a widespread tendency, which the reviewer regards as unfortunate, to neglect not only the cultural but also the laboratory aspect of the science, Professor Weeks's work appears to him to be of great and timely educational value. The reviewer believes that the book ought to be read and absorbed by every teacher of general chemistry, in high school and university. Incidentally, the book might prove of interest to mineralogists and geologists as well as to chemists, because of the intimate connection between mining and the discovery of the elements, especially in the eighteenth century.

Owing to its sense of the existence of relations between chemistry and its cultural matrix, Professor Weeks's book is a true synthesis. Nevertheless the book fails to realize to the full the possibilities for synthesis inherent in its subject matter, and this constitutes, for the reviewer, the chief criticism that can be made of the work. The failure consists in a lack of explicitness regarding the relation between the history of the discovery of the elements and the history of chemical ideas in general.

One important connection between the history of the elements and the history of chemical ideas lies in the series of profound changes undergone by the concept of element itself—changes of which the end is not yet in sight. Save for some fragmentary remarks on page 3, the author says nothing about this. Boyle's celebrated definition of element is never mentioned. Did he apply it at all, and do we know what he thought about phosphorus in this regard? What meaning, if any, is to be attached to the concept of "principle" as distinct from that of element? What ideas on the concept of element were held by the pre-Lavoisierian discoverers of the eighteenth century, who were all more or less under the spell of phlogiston, and how were these *ideas* related to their *discoveries*? The author quotes Lavoisier's table of thirty-three elements (p. 202), but does not consider it worth while to point out that this table represents the first *systematic* attempt to apply Boyle's definition, that for about a century after Lavoisier the substances called elements were generally believed to correspond to Boyle's definition, but that more recently, owing to the periodic law, the electron, radioactivity, isotopes, etc., this belief was recognized as erroneous and that at present it seems at least doubtful whether anything corresponding to Boyle's definition exists at all.

Another important link between the history of the elements and the history of chemical ideas is the question as to how the major advances in chemical method, law and theory have contributed to the discovery of elements. Professor Weeks, to be sure, makes it abundantly clear that the voltaic cell and the spectroscope led to new elements, that Mendeleef's predictions from his periodic law were a stimulating factor, and that advances in our knowledge of atomic structure

were responsible for the discovery of hafnium. She also indicates, though somewhat less clearly (pp. 62–63, 201–202), that the systemization achieved by Lavoisier was important for the discovery of certain elements. But the general question is left untouched. Why, for instance, have certain gains in theory led to new elements immediately, while others, such as Dalton's atomic theory, apparently not?

Perhaps Professor Weeks has felt that these and similar questions are best left to the histories and texts of general chemistry. As far as a *complete* discussion is concerned, the reviewer would concur in this opinion. He believes, however, that more attention to such questions would have resulted in a significant increase in the value, already great, of Professor Weeks' work.

F. O. KOENIG

STANFORD UNIVERSITY
CALIFORNIA

LECTURE DEMONSTRATION OF X-RAYS AND CATHODE RAYS

CHARLES L. CHRIST *Wesleyan University, Middletown, Connecticut*

ALTHOUGH it is generally realized that well-planned demonstrations of the production and properties of cathode rays and X-rays lend very effective aid to the teaching of these subjects, many institutions have had to forego these because of the prohibitive cost of the necessary apparatus. Such equipment, consisting of an induction coil, X-ray tube, Crookes tubes, magnet and fluoroscope, all designed specifically for demonstration purposes, and obtained from the laboratory supply houses costs at least $250.

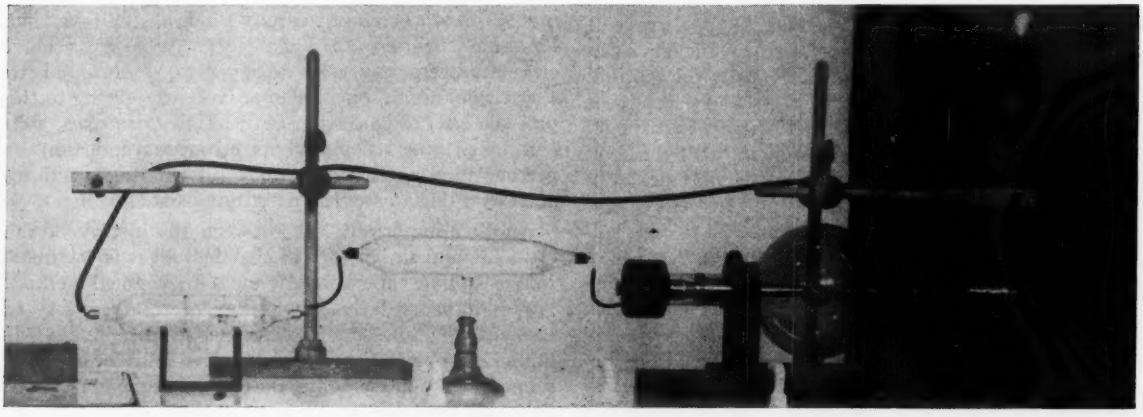
To meet this difficulty, we have taken advantage of the fact that obsolete X-ray medical equipment may be obtained from X-ray dealers at prices appreciably less than that asked for new standard demonstration apparatus. The apparatus described below is, with the exception of the two Crookes tubes (low cost items), composed entirely of such inexpensive obsolete pieces. It has been found to give highly satisfactory results.

The figure shows the setup, consisting of two Crookes tubes and a Coolidge type X-ray tube in series. The three tubes are energized as a unit by a high-voltage oil-immersed transformer, which contains a built-in filament transformer for lighting the filament of the Coolidge tube. The apparatus is operated at a potential of 80,000 volts and a current of 1 milliampere, the high voltage and current being controlled by means of an auto-transformer and a resistance, respectively, connected in the primary circuit and housed in a control stand. The high tension lines may be carried safely by clean wooden funnel supports, as shown.

In this setup the Coolidge tube plays a dual role. It is used both for the production of X-rays and as a valve tube for the rectification of the electron beams produced in the Crookes tubes. It was found that the electron beams produced in this way were much sharper than those produced through the use of an induction coil. In the X-ray experiments a square of Patterson Type B fluorescent screen serves very well as a fluoroscope. Experiments showing the charge and the kinetic energy of the electron beams are carried out in the usual way.[1]

It is a pleasure for the author to acknowledge his indebtedness to Mr. J. W. Moulton of the General Electric X-ray Corporation. Thanks are also due to Dr. M. G. Burford, of this laboratory, for the photograph used in this paper.

[1] ARTHUR, "Lecture demonstrations in general chemistry," McGraw-Hill Book Company, New York, 1939, p. 237.



CROOKES TUBES AND COOLIDGE TUBE, CLOSE UP

Report of the
NEW ENGLAND ASSOCIATION
of CHEMISTRY TEACHERS

The Structure of Atomic Nuclei[1]

ROBLEY D. EVANS *Massachusetts Institute of Technology, Cambridge, Massachusetts*

INVESTIGATIONS of the structure of atoms have shown that each atom possesses at its center a small, dense, positively charged core or nucleus. Outside the nucleus the atom consists only of a swarm of negative electrons just sufficient in number to balance the positive charge on the nucleus, so that the complete atom is electrically neutral. It is possible to modify the structure of atomic nuclei to produce new atoms having unusual properties. In many cases these artificial atoms are radioactive and can be usefully applied in engineering, physics, chemistry, geology, and medicine.

A glass of water contains about 20 million million million million atoms. If we were to enlarge the scale to make the glass so big that it would contain the entire earth, we should find the individual oxygen atoms to be about one inch across. The hydrogen ions (protons) would be too small to see. Further examination of the 1-inch oxygen atoms would reveal very little, for we should find each of them to consist of a nucleus and a small number of electrons, the dimensions of each of these particles being only a few millionths of an inch. Thus the atom is mainly empty space, but it retains its shape and its volumetric displacement by virtue of its very strong internal electric fields. To be able to see anything in our glass of water we must again expand the scale. We must make it so big that the sun could be placed at its center and still allow the planets Mercury, Venus, and the Earth to traverse their regular orbits about the sun with plenty of room inside the glass. We could then see the individual particles which comprise the atom. If, for example, we chose to examine an oxygen atom in the water, we should find it to be a roughly spherical object having a diameter of about 10 miles. Occupying this 10-mile spherical space we should find a nucleus at the center and 10 electrons revolving about it at distances up to five miles, each of these eleven particles being only about the size of a grapefruit. Only the very outermost electrons, at the edge of this 10-mile sphere, are involved in ordinary chemical and biochemical reactions. The inner electrons and especially the atomic nucleus remain relatively unaware of the activity of the outer electrons of the atom.

We may now go to the center of this 10-mile oxygen atom and examine the nucleus. Close inspection would show the nucleus to be a closely packed group of individual particles, like a bunch of large grapes. The oxygen nucleus, if we had maintained its density constant during our expansion of its dimensions, would weigh 500,000 million tons. It would consist of 16 closely packed particles of two types. There would be eight particles, called "protons" each having unit positive charge. There would be eight more particles of substantially the same size and mass as the protons, but having no charge. These neutral particles are called "neutrons." These neutrons and protons are very much alike, and when it is conducive to the formation of a more compact and stable nucleus, neutrons are actually capable of changing themselves into protons and vice versa. Thus the neutron and proton may be regarded as alternate aspects of one fundamental but unnamed nuclear particle. There appear to be no other particles aside from protons and neutrons in the nucleus.

If we examine a large number of oxygen nuclei we shall find a few rare ones which contain 17 particles and others which contain 18 particles in the nucleus. Each of these nuclei contains eight protons, hence has a positive charge of eight units, and requires eight electrons, within the 10-mile sphere that is our neutral atom or 10 electrons in the oxygen ion of the water molecule. Since the chemical properties are dictated by the number and configuration of the electrons, chemically all these atoms will behave identically. They are therefore called "isotopes," and occupy the same place in the periodic table. Since nearly all of the mass is concentrated in the atomic nucleus, because of the relative lightness of the electrons, these three types of oxygen atoms will have different atomic weights. All of the 278 known stable isotopes of the

[1] Abstract of an address presented at the Fourth Summer Conference, University of New Hampshire, Durham, N. H., August 13, 1942. Some of the material discussed by Dr. Evans was published in an article in the June, 1941, issue of *Electrical Engineering*, to which we are indebted for permission to reproduce the cut.

Courtesy of Electrical Engineering

FIGURE 1.—DIAGRAM SHOWING ALL THE ATOMIC NUCLEI OCCURRING IN NATURE

92 chemical elements differ from one another only in the number of neutrons and protons in their nuclei, and in the configuration of the accompanying electrons.

In nuclei, the neutrons play the role of a binding cement which holds the entire nucleus together, in spite of the very strong electrostatic repulsive forces which the positive protons exert upon one another. Thus in the heavier nuclei we find a slightly larger proportion of neutrons in the nucleus in order to overcome the rapidly mounting repulsive forces between the larger number of protons. The most complicated nucleus is the heaviest and most common isotope of uranium. This nucleus contains 92 protons and 146 neutrons, making a total of 238 particles, yielding thus an atomic weight of 238. Uranium, like several other heavy elements, does not have a completely stable nuclear configuration, possibly because of its excess weight and complexity. It can become more nearly stable by splitting off from itself a helium nucleus (alpha particle), 2 protons and 2 neutrons, and expelling this fragment. This is the origin of the alpha-ray radioactivity of heavy elements. In addition, some of its neutrons are converted into protons by the emission of electrons (beta rays). It becomes stable only after it has ejected a total of eight alpha particles and six electrons and an isotope of lead is finally produced.

Figure 1 is a plot which shows each of the known stable nuclei as a square. The vertical coördinate represents the atomic number, Z, that is, the number of protons in the nucleus. The horizontal coördinate is a compressed scale of mass numbers, or atomic weights, A. The quantity actually plotted is $A-2Z$, that is, the number of excess neutrons over and above the number which is just sufficient to equal the number of protons in the nucleus. These nuclei appear to represent all the stable configurations that can be made by taking an arbitrary number of protons and adding neutrons in such numbers that stable nuclei result. The few naturally occurring radioactive isotopes are shown as circles. Moreover, it will be noticed that even light elements like potassium, 19, rubidium, 37, and samarium, 62, have unstable isotopes. A number of gaps appear in the horizontal groups of isotopes, from which we can infer that these positions represent unstable arrangements and that if such nuclei were synthesized in the laboratory, they would be radioactive; that is, spontaneously transform themselves into more stable configurations. Such transformations are called "artificial radioactivity." The word "artificial" is used only to remind us that the nuclei in question are not found in nature, but have been produced in the laboratory. Over 350 artificial radioactive isotopes have been produced to fill gaps, to the right, in between, and to the left of these stable isotopes.

RECENT BOOKS

OPTICAL METHODS OF CHEMICAL ANALYSIS. *Thomas R. P. Gibb, Jr.*, Ph.D., Instructor in Analytical Chemistry, Massachusetts Institute of Technology. First Edition. McGraw-Hill Book Company, New York, 1942 (International Chemical Series). xiv + 391 pp. 300 figs. 16 × 23 cm. $5.00.

"The purpose of this book is to present a compact, abridged survey of the field of optical methods of analysis, in a style suited both to the practical analyst and to the advanced student of analytical chemistry. . . ." The book is arranged as a text with a chapter devoted to each optical method and its uses: Spectrochemical Analysis; The Spectrophotometer; The Colorimeter, Turbidimeter, Nephelometer, and Fluorophotometer; The Microscope; Elementary Crystallography; Identification of Crystals with the Polarizing Microscope; The Refractometer; The Polariscope. Extensive bibliographies of leading references, and lists of provocative problems on each of these topics are supplied, as encouragement to further study.

"The author has emphasized the design and manipulation of instruments rather than the theoretical aspects of the subject, but has endeavored to present whatever theoretical considerations are necessary for intelligent application of the methods discussed." This spares the reader some abstruse physical optics, but leaves him plenty to chew upon, for the book avoids being primarily a manual of directions for experiments, nor is it padded with rewritten manufacturers' descriptions of apparatus; instead, the discussions of instruments are generalized and critical and the theory of the methods is presented in a simple and logical manner.

The author states that the tutorial system is employed throughout his own laboratory classes. This is almost essential, in the reviewer's opinion, because of the inherent complexity and diversity of the subject matter of the field, and because the author has not "written down" the book to the level of an ordinary laboratory manual. Its style will appeal to the intelligent student and the independent mature worker, but it does not offer a fool-proof automatic guide for a perfunctory course in "instrumental methods." In fact, prospective users of this book for teaching are advised to work through those problems in each chapter, well ahead of the class; the answers won't be found just by looking in the index.

C. W. MASON

CORNELL UNIVERSITY
ITHACA, NEW YORK

EQUILIBRIUM AND KINETICS OF GAS REACTIONS. AN INTRODUCTION TO THE QUANTUM-STATISTICAL TREATMENT OF CHEMICAL PROCESSES. *Robert N. Pease.* Princeton University Press, Princeton, New Jersey, 1942. ix + 236 pp. 16 figs. 15 × 23 cm. $3.75.

This book fills admirably a real need. The first sentence in the preface reads, "This text has developed from a course of lectures given to a group including seniors, first-year graduate students and fifth-year chemical engineers." Such students are provided with a sound introduction to an important field. After a good course in physical chemistry they should be able to follow this text into the modern interpretation of chemical processes. From it they should obtain an appreciation and considerable critical knowledge of this branch of chemistry in which extremely important theoretical developments have been made recently, but in which even the experimental data must still be closely examined. Another group, those who have been out of contact with recent developments in gas reactions, and whose interests the author has in mind, should find the book of great value.

The first part of the book is devoted to Chemical Equilibrium. The necessary thermodynamics is included simply and concisely. The notions of quantum theory and statistics are introduced in a clear, practical fashion. In Part Two the theories of reaction rate are presented in very sensible fashion and followed up with a good selection of experimental studies. After a discussion of the more conventional classes of reactions, chapters on chain reactions, explosions, and surface reactions are included.

A wisely generous number of tables and plots of data are given throughout the book. Unfortunately the diagram on page 92, if removed from context, would be misleading. It is to be hoped that the reader will not think the plot to be typical of potential energy diagrams of diatomic molecules.

The author deserves commendation for his choice and presentation of material for the purpose he had in mind.

JOHN P. HOWE

BROWN UNIVERSITY
PROVIDENCE, RHODE ISLAND

INTRODUCTORY COLLEGE CHEMISTRY. A Course for Beginners. *Horace G. Deming*, Professor of Chemistry, University of Nebraska. Second Edition revised in collaboration with *B. Clifford Hendricks*, Professor of Chemistry, University of Nebraska. John Wiley and Sons, Inc., New York, 1942. xii + 527 pp. 176 figs. 15 × 23 cm. $3.00.

The authors of this text have made a careful and thoughtful selection of subject matter. Not only have the older and outmoded industrial applications of chemical principles been replaced by modern methods, but newer explanations are substituted for the older and rather inadequate ones.

The modern concepts of acids and bases, atomic structure, valence linkages, indicators, of radioactive change, and others are so clearly and skilfully presented that the average student should find the mastery of the subject matter decidedly interesting and not at all beyond his comprehension. The authors have, quite wisely, presented some comparisons between a number of the newer and the older ideas, so that one may more readily understand and appreciate the earlier points of view.

The chapters on Organic Synthesis and on The Chemistry of Nutrition are particularly well done and worthy of comment. Figures are almost without exception clear, instructive, and stimulating.

The second edition has retained many of the desirable features of the first. Notable among these are: the principle of first presenting involved topics in a simple form, then reviewing, enlarging, and developing them in later chapters; closely associating uses of substances with their properties; numerous questions at the ends of the chapters, which stimulate reflective thinking and require a thorough understanding of the chemical principles involved, rather than a regurgitation of the facts.

The authors have come very close to realizing all of their objectives for this text, stated and implied in the preface and conclusion.

ALLEN R. HARTZELL

THE ST. LAWRENCE UNIVERSITY
CANTON, NEW YORK

ACID-BASE CATALYSIS. *R. P. Bell.* The Clarendon Press, Oxford, England, 1941. viii + 211 pp. 22 figs. 13.8 × 21.5 cm. $3.50.

A physico-chemical monograph which reaches its culmination in the discussion of the mechanism of acid-base catalysis and its relation to chemical kinetics. At a more elementary level Chapter 3, dealing with modern views on acids and bases, and Chapter 2, on salt effects and the modern general ionic theory, will make good reading for teachers who want to bring themselves up to date in this field.

LIEBIG AND AFTER LIEBIG. A CENTURY OF PROGRESS IN AGRICULTURAL CHEMISTRY. Edited by *Forest Ray Moulton*. Publication Committee: *Charles A. Browne*, Chairman, *Richard Bradfield*, and *Hubert B. Vickery*. American Association for the Advancement of Science, Washington, D. C., 1942. 111 pp. 15 figs. 18.8 × 26 cm. $3.00; to members of the A.A.A.S., $2.50.

This volume is best characterized in the words of Dr. F. R. Moulton in his Foreword:

"Like other symposia published by the Association, this one not only reviews an extensive literature, but describes current opinions and practices and new methods of investigation that are now being developed. The dramatic story is told of the profound revolution in agricultural science that was brought about by the dominating leadership of a most gifted, yet often mistaken, chemist; by the polemics that were aroused by the fierce hostility of his criticisms; by the world-wide propagation of his doctrines through his numerous books and popular writings, and by the many loyal pupils of his school; and by his great influence in opening up new fields of knowledge in soil science, in plant and animal nutrition, and in the theory and manufacture of chemical fertilizers. As in other scientific developments, each discovery in these various subjects has raised an ever-widening variety of new problems. The book closes with a broad and well-documented survey of plant nutrition experiments by means of solution culture, a procedure that still promises to be the surest road to sound basic conclusions."

A SHORTER COURSE IN ORGANIC CHEMISTRY. *J. C. Colbert*, Associate Professor of Chemistry, State University of Oklahoma. Second Edition. D. Appleton-Century Co., Inc. New York, 1942. xvii + 355 pp. 14.8 × 22.4 cm. $3.75.

This book is designed for a one-semester course in organic chemistry, though the author states that it is not possible to cover more than one-half to two-thirds of the text in a one-semester course. There is a detailed discussion of aliphatic compounds, followed by a well-condensed discussion of aromatic compounds and a chapter on heterocyclic compounds.

The reviewer is very skeptical of the value of the brief discussion of structural isomerism, tautomerism, optical isomerism, and geometrical isomerism in the introductory chapter. The nomenclature does not agree with that used by most organic chemists, as shown by such names as 4-iodobutane, 2-hydroxybutanal-4 and methyl nitrile. There are several errors which are indicative of careless proofreading. For the most part, chemical reactions are represented correctly, though the reviewer is not aware of any reaction between acetic acid and acetyl chloride to form acetic anhydride (p. 125), and certainly maltose does not form glucose and fructose when hydrolyzed (p. 77).

The book contains some excellent charts showing the relationships which exist among various compounds, and the suggestions to the student at the end of several of the chapters are good. The comprehensive review chapter of aliphatic compounds (14 pp.) will be helpful to students.

J. PHILIP MASON

BOSTON UNIVERSITY
BOSTON, MASSACHUSETTS

A MANUAL FOR EXPLOSIVES LABORATORIES. *G. D. Clift*, Chief Chemist, and *Dr. B. T. Fedoroff*, Research Chemist, Triton Chemical Company, Glen Wilton, Virginia. Lefax, Inc., Philadelphia, 1942. 202 pp. 8.5 × 17 cm. $2.00.

With the increasing demand on the Military Explosives Industry of the current war effort, has come the necessity for training chemists as specialists in explosives. The authors have published methods and modifications used in their own laboratory to assist in this training program, feeling that laboratory secrets should be dispensed with in an emergency. The book is published in handy loose leaf form, allowing the addition of sheets as they are issued, as well as ease in the addition of revisions and personal notes.

LIVING CHEMISTRY. *Maurice R. Ahrens, Norris F. Bush, and Ray K. Easley*. Ginn and Company, Boston, 1942. xvii + 528 pp. 21.6 × 26 cm. $2.28.

This textbook, new in size and organization, was written by three men, all of whom have taught chemistry in the Denver public schools. The most unusual feature of the text is its organization. Part I, the "Fundamentals of Chemistry" appears to be an abbreviated chemistry course, including the basic principles "necessary to give pupils enough background to make possible a direct attack upon the meaningful problems which are related to chemistry." The next three parts include practical application plus some "additional facts and concepts," and these sections are labeled: "II. Chemistry of the Individual"; "III. Chemistry of the Home"; "IV. Chemistry of the Community." The last three sections deal with an interesting array of practical applications in which chemistry plays a most important part. These areas include fuels, foods, refrigeration, gardening, water purification, sewage disposal, various industries, and warfare. While these topics are discussed in a very interesting manner, the actual chemistry of the whole section has evidently been left largely for the teacher and the references to explain. After giving the students a background of chemistry, it seems to this reviewer that the authors might safely have inserted more chemistry and explanation into the latter sections. There are relatively few pages in these "applications" that could not be understood by a pupil who knew only that there were such things as chemical formulas.

The authors claim to have developed this organization through about twelve years of experimentation, and say that they "have evidence to show" that their type of organization is practical and usable. Those of us who have worked with new courses of study would be more impressed by references which in turn would show just what the authors have done to prove the wisdom of this unique organization.

The style and exposition is certainly not too difficult for the average high-school student, and numerous thought questions have been scattered throughout the sections. Considerably more attention has been given to biological and hygiene problems than is common to most chemistry textbooks. The book is organized under the unit plan, and contains numerous tests and unit exercises. The references at the end of the sections, with one or two exceptions, include books, pamphlets, and periodicals, but include no reference to specific articles in the current journals and magazines. For a text which the pupils are said to have had a part in developing, it is strange that there are no page and volume references to specific current articles.

This textbook is a commendable addition to the large array of high-school textbooks now available, and the authors are to be congratulated upon a successful effort that neither reflects nor perpetuates the conventional and traditional patterns of the last *umpteen* years.

SHAILER PETERSON

SOUTH DAKOTA STATE COLLETE
BROOKINGS, SOUTH DAKOTA

WAR GASES. *Morris B. Jacobs*. Interscience Publishers, Inc., New York, 1942. xiii + 180 pp. 14.5 × 22.5 cm. $3.00.

This is an excellent contribution to the rapidly increasing literature of civilian defense. While written especially for the gas identification officer, the war gas chemist, the decontamination officer, and the health officer, it nevertheless should prove of value to the air raid warden and in general to anyone having an actual—or imagined—relation to gas defense.

The classification and properties of chemical agents, as well as the methods of decontamination, are effectively dealt with. One chapter is concerned with a topic too often neglected: the effect of war gases on materials, water, and food. But nearly half the book deals with the subject of detection and analysis of the chemical agents, and much analytical information of interest and value to the chemist will be found in this section. Many sources have been drawn upon, including the analytical literature, government bulletins, and standard references and texts.

EXPLOSIVES. *John Read.* Published by Penguin Books Limited, Harmondsworth, Middlesex, England, 41 East 28th Street New York, 1942. 160 pages. Illustrated. 11 × 17 cm., paper covers.

This is one of the Pelican Books (published by Penguin Books Limited) which are on sale throughout England at the moderate price, as we understand it, of six pence each. The price of the book is not marked upon it. Advisory Editors of the series are H. L. Beales, Reader in Economic History, University of London, and W. E. Williams, Secretary of the British Institute of Adult Education. The author, Professor of Chemistry in the University of St. Andrews, is well known to readers of this JOURNAL. His name is a guarantee that the book is authoritative in substance and wholly understandable, pleasing in style, easy and entertaining to read. It is written in a popular manner, journalistically, to convey a sympathetic understanding of the subject of explosives to a reader who has had no previous acquaintance with chemistry. We say *sympathetic* because it will make the reader realize that explosives serve many friendly purposes, that they are powerful civilizing influences—good for much else besides the killing of men. We say *understanding* because, without technicalities, it makes apparent the relationships of explosives to the general economy of the times, to fats, to cotton, to coal, and to the gases of the atmosphere.

The author's dedication is "1242–1942 to a future which shall see 'the marvellous power of art and of nature,' as foreshadowed by Roger Bacon, ranged wholly on the side of humanity."

The author's sense of humor and the rightness of his insight are both illustrated by the following typical passage, chosen almost at random. "Reverting now to the picture of carbon atoms as diminutive four-handed beings, it can be said that their social activities are unrivalled in the whole world of atoms. This is due only in part to their four-handed nature, because there are other kinds of atoms having as many as six or seven hands and yet endowed with only a rudimentary social instinct. The unique characteristic of carbon atoms is their unequalled capacity for fraternising among themselves. Atoms of other elements exhaust their powers of mutual hand-clasping by the time that three or four of them, at the most, have joined in. Carbon atoms, on the contrary, enter into this form of association with the utmost zest, keeping at the same time their friendly contacts with other atoms, notably those of hydrogen, oxygen, and nitrogen."

And another passage. "If animals were able to assimilate petroleum, life would perhaps be speeded up unpleasantly even for an age that makes a fetish of speed. Nature abounds in common sense. . . .

"In her chemical mood, indeed, Dame Nature is a benign mother. Not content with endowing man with rich chemical storehouses of food and energy, she has savoured his dishes with salt and spices, delighted his eyes with bright colours and his nostrils with fragrant perfumes, and has clothed him in garments of fibrous cellulose and proteins—her cottons and wools and silks. She has ordained, with a care hardly less than grandmotherly, that no natural beverage shall contain more than about 15 per cent of alcohol; and even her poisons—her strychnine and morphine and atropine—have their beneficial uses. Finally, in her wisdom, she has refrained from including in her lavish chemical cornucopia any substance of an explosive nature. . . .

"Explosives are purely artificial productions. . . .

"In his first successful attempts to make an explosive, Nature's wilful child mixed two combustible materials, charcoal and sulfur, with another substance, saltpetre, containing an abundance of oxygen in a condensed or combined form. . . .

"Not content with the power of his first explosive—gunpowder—man has turned to the concentrated organic energy of the carbohydrates, fats, coal, and petroleum, in fabricating the enormously powerful explosives of modern times. Into the molecules of substances derived from these sources, so stable and peaceful in their natural form, he has introduced a potential disintegrating influence in the form of nitro-groups (—NO_2). These nitro-groups infect the molecules with instability, by virtue of the relatively loose attachment of their constituent oxygen and nitrogen atoms. Nitro-groups are the fifth columnists of the molecular world. When the proper moment arrives they bring about the complete collapse of the molecular society into which they have insinuated themselves."

In a small and popular book of this sort it is perhaps remarkable that so many of the most recent developments in the explosives art should be mentioned at all. The author does not discuss nitroguanidine, but does touch upon flash reducers, cooling agents, and moderants or deadeners for smokeless powder, on hexamethylenetriperoxidediamine (HMTD), on trinitrotriazidobenzene, on tetracene, and on "Cyclonite, also known as Hexogen or T4." The book will help to make many persons understand more clearly these essentially benevolent substances which have lately been elected to fulfil for a time the roles of assassin and murderer.

TENNEY L. DAVIS

NORWELL, MASSACHUSETTS

EMULSIONS AND FOAMS. *Sophia Berkman and Gustav Egloff,* Universal Oil Products Company, Chicago. Reinhold Publishing Corporation, New York, 1941. viii + 591 pp. 40 figs. 15 × 23 cm. $8.50.

This very useful book naturally contains an extensive section on petroleum emulsions since the authors are chemists in that field. They make the astounding statement that one-fourth of all the petroleum obtained in the United States carries emulsified water. Some pipe line companies refuse to transport oil containing over two per cent water, and a few set the permissible limit as low as one-half per cent. Many of these water-in-oil emulsions are difficult to break, so there has developed much patent literature on the subject, ably discussed by Berkman and Egloff. The practical side of testing such emulsions is, quite properly, given adequate attention.

Eight types of "demulsification" are listed: topping, heat treatment, chemical treatment, desalting, freezing, filtration breaking, electrical dehydration by alternating current, and centrifuging. Of these the chemical and electrical treatments and heat treatment under pressure are in most common use.

The five chapters deal with: (1) The Theory of Emulsions and Foams, (2) Practical Knowledge of Emulsions (Emulsification), (3) Demulsification, (4) Asphalt and Bitumen Emulsions, (5) Laboratory Methods Used in the Examination of Emulsions.

It is interesting to note the extensive use of the asphalt type of emulsions for paints, roofing, pipe covering, and road surfacing.

Froths and foams, surface tension effects, viscosity, volume relations, electrical charge, hydration of emulsifying agents, and orientation of films are well treated. This book will be very helpful to all workers in the emulsion field.

HARRY N. HOLMES

OBERLIN COLLEGE
OBERLIN, OHIO

FLUORESCENT CHEMICALS AND THEIR APPLICATIONS. *Jack De Ment,* Research Chemist, The Mineralogist Laboratories; Associate Editor, The Mineralogist Magazine. With a special chapter on Ultraviolet Radiation Sources by *H. C. Dake,* Editor, The Mineralogist Magazine. Chemical Publishing Company, Inc., Brooklyn, New York, 1942. xiii + 240 pp. 11 figs. 13.7 × 21.7 cm. $4.25.

In a listing of nearly 3000 chemicals and their fluorescence, the author has included many new chemicals, some of which are comparatively rare. The chief concern of the book, aside from the extensive listing, is a presentation of the uses of fluorescent chemicals in the industries, arts, and sciences. A brief discussion of the fundamentals, and the basis for fluorescence analysis are included for the sake of clarity. The present volume follows a previous work, "Fluorescent Light and Its Applications," written with H. C. Dake.

Of particular interest is a study of the action of beta and gamma rays on water, with the production of abiotic ultra-violet light. Attention is directed by the author to the interpretations, possible from this study, of the lethal action radioactive substances exert on neoplasms, and the destruction these agents cause in normal tissues.

ELEMENTARY PHYSICAL CHEMISTRY. *Merle Randall*, Professor of Chemistry, University of California, Berkeley, California, and *Leona Esther Young*, Professor of Chemistry, Mills College, Oakland, California. Randall and Sons, 2512 Etna Street, Berkeley, California, 1942. xiv + 455 pp. 279 figs. 15 × 23 cm. $4.50.

The authors wrote this book primarily for sophomore and junior students and particularly for those not majoring in chemistry. To arouse interest, applications are stressed in both illustrations and problems. As a further stimulus, "The order of presentation is arranged to parallel the work . . . in . . . several courses beyond the first year." This results in an outline somewhat as follows: Introduction, vaporization and activity, quantitative analysis, fugacity and perfect solutions, general ionic equilibria, gases, thermochemistry, liquid mixtures, colligative properties, phase rule, free energy, electromotive force, volumetric relations, solubility and activity, special ionic equilibria, viscosity, conductivity, polarization, kinetics and radioactivity. Moreover, the various subjects are so interwoven that selection of chapters alone will not suffice to fit the book to the more traditional order. The book is called "elementary" and in part it is. But the reader may question the justification for using this term when he considers the twelve pages spent on kinetic theory, sixteen more on the solubility of "insoluble" salts, and other things of like character.

In its parts the book is well written and interesting. Especially well done are the sections on ionic equilibria, indicators and buffers, free energy and equilibrium, phase diagram interpretation, etc. As might be expected, the thermodynamic approach is emphasized throughout. The solution of problems by the method of successive approximations is carefully demonstrated in several connections. There is an unusually extensive discussion of calorimetry. Six hundred and ninety-four problems provide a most liberal collection. Each of the numerous figures is accompanied by an explanatory paragraph. There are abundant references and ample tables of data (96, including those in the problems and appendix). The book is a photolith reproduction.

This book is recommended for reference purposes, for individual study, and as a text when the conditions of its use approximate the authors' intentions.

MALCOLM M. HARING

UNIVERSITY OF MARYLAND
COLLEGE PARK, MARYLAND

ANALYTICAL CHEMISTRY, VOLUME II. QUANTITATIVE ANALYSIS. Based on the text of *F. P. Treadwell*, revised and enlarged by *William T. Hall*, Massachusetts Institute of Technology. Ninth English Edition. John Wiley and Sons, Inc., New York, 1942. xi + 808 pp. 121 figs. 15 × 23 cm. $6.00.

Since 1904 when the first English edition of this text appeared, the book has been a standard reference work for analytical methods. During the last four decades there have been few students of quantitative analysis who did not seek and find valuable analytical methods in the Treadwell and Hall.

It is significant that there is a Ninth Edition to review and this, in itself, speaks for the value and importance of the book. This edition is certainly not a translation of the German text, and it is more than a revision of the eighth English edition. Professor Hall has expanded many parts, introduced new methods, completely rearranged the sequence of metallic elements, and yet, by elimination of some of the older material, has kept the size of the book practically the same as in previous editions. This is in accord with the author's purpose to have it "an inexpensive textbook, which is meant to be useful to students of chemistry who desire precise information concerning well-known analytical methods." As in previous editions the author has limited himself to the methods of Gravimetric, Volumetric (Titrimetric), and Gas Analysis. These constitute three of the four parts of the book. The fourth part is composed of informational and useful data, as density tables of acid and base solutions, molecular and equivalent weights, chemical factors based on 1941 atomic weight values, and logarithm tables. The application of instrumental methods to analysis is definitely excluded from the scope of the book, and micro and semimicro methods have not been included.

A major change is the rearrangement of the cations according to the usual scheme of qualitative analysis. As in previous editions most of the analytical theory is relegated to "Volume I. Qualitative Analysis," but the essential theoretical material for acidimetry and alkalimetry is given and the Brönsted concept of Acid-Base is introduced. The theory relating to indicators, buffer solutions, and oxidation-reduction has been expanded.

The section on weighing and manipulative technic is definitely improved by the replacement of the Kohlrausch method of weight calibration by a transposition method, by the elimination of some figures representing old type equipment, and by the introduction of a brief discussion of colloidal solutions and coprecipitation.

This edition retains all the advantages of the previous editions, and in addition has brought in some newer analytical methods. The use of the term "polarity" (p. 449) affects this reviewer very much as the same usage affected the reviewer of Professor Hall's "Textbook of Quantitative Analysis."[1] The reviewer regrets too that a considerable number of references are given without the year, thereby making it difficult for the reader to determine quickly the applicability of a given method to a present problem. The book is an excellent reference text for advanced analytical students, teachers, and investigators. It also serves most admirably as a reference book for beginning analytical students because it offers a variety of methods for a given determination and therefore gives definite training in choice of analysis. The details of procedure are clear cut and accurate. The book is well arranged, the type, paper, and binding excellent. It will be welcomed not only by those who have consistently used the preceding editions but by the younger analysts who are beginning to realize that the choice in method of analysis depends not alone on the constituent sought but on many other factors.

MARY L. SHERRILL

MOUNT HOLYOKE COLLEGE
SOUTH HADLEY, MASSACHUSETTS

AN OUTLINE OF ORGANIC NITROGEN COMPOUNDS. *Ed. F. Degering*, Purdue University; *Carl Bordenca*, Alabama Polytechnic Institute; and *G. H. Gynn*, Westvaco Chlorine Products Company. Third Edition. John S. Swift, Inc., Cincinnati, Ohio, 1942. 381 pp. 15 × 23 cm. $6.00.

This book represents in planographed form material accumulated by the authors over a period of many years, and in part included in courses given at Purdue University. It follows in general the type of "Outlines of organic chemistry" by Degering, Nelson and Harrod, and although written in outline form it nevertheless contains enough discussion and explanation to permit of its use as a textbook. One may also add that it will make a very useful reference work of moderate size in this field.

The first chapter, entitled "General Concepts," deals with questions concerning atomic structure, relative electronegativity, and the mechanism of reactions. There follow a few pages on the fixation of nitrogen and the ammonia system, and then an extended treatment of the more important classes of open chain nitrogen compounds (242 pp.). Alkaloids are treated briefly (12 pages) and nitrogen ring compounds somewhat more fully, though here only the methods of preparation are given. The book concludes with short sections on explosives and on the isomerism of organic nitrogen compounds. The arrangement of a typical section (aliphatic amines) is the following: *A.* The general relationship of the amines and their natural occurrence; *B.* Nomenclature; *C.* Preparation; *D.* Physical Properties; *E.* Reactions.

The printing, typography and binding are good, although the reviewer has noticed a few minor misprints. The price seems a trifle high for a planographed book of this size.

F. W. BERGSTROM

STANFORD UNIVERSITY
CALIFORNIA

[1] HALL, J. CHEM. EDUC., **19**, 350 (1942).